DETAILED STUDY OF THE REACTION MECHANISM OF SPONTANEOUS COMBUSTION OF COAL WITH PARTICULAR EMPHASIS ON WESTERN CANADIAN LOW-RANK COALS

PHASE II

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FINAL REPORT
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THE UNIVERSITY OF CALGARY
CALGARY, ALBERTA

Detailed Study of the Reaction Mechanism of Spontaneous Combustion of Coal with Particular Emphasis on Western Canadian Low Rank Coals.

Phase II

A Report by

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Dear Dr. Chakravorty:

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We take pleasure in submitting our final report on Phase II of our study on the mechanism of spontaneous combustion in Western Canadian low-rank coals. We would like to thank the Coal Research Laboratories of CANMET for sponsoring this study and for their advice and guidance throughout the term of this project.

Respectfully submitted,

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/ds

Enclosure

SUMMARY

This project was carried out under the auspices of the Coal Research Laboratories of CANMET to study the effect of drying Western Canadian coals on their susceptibility to spontaneous combustion. These effects were studied by measuring thermal responses of the dried coals to moist air treatment, and by measurements of changes in porosity and surface area, peroxygen content and free radical content. In addition, an update on the review of spontaneous combustion of coal with emphasis on the above parameters has been completed.

Six Alberta coals were selected for this study. These included three foothills coals of high volatile bituminous rank, and three prairie coals of subbituminous rank. All coals were submitted for petrographic, proximate, ultimate and trace metal analysis. Moisture contents in the high volatile bituminous coals ran from seven percent to twelve percent, while those of the subbituminous coals ran from eighteen to twenty five percent. The oxygen content of the dry ash-free coals generally followed with rank, the high volatile bituminous coals having less than the subbituminous coals.

All coal samples were crushed and sieved. A number of each of the samples were then dried so that samples of moisture content decreasing by one to two percent were obtained until a moisture content of less than fifty percent of the equilibrium moisture was reached. Each of these dried samples was then treated with flowing 60% relative humidity air in an adiabatic calorimeter for three hours and the temperature response measured. With one exception, all coals showed negative thermal responses when they still had a moisture content between seventy to eighty percent of equilibrium moisture. Below seventy percent equilibrium moisture content all coal samples showed positive thermal responses. The three high volatile bituminous coals showed

very similar thermal rises as moisture content decreased, whereas the subbituminous coals showed a wide variability in their thermal responses.

Peroxide contents of moisture equilibrated high volatile bituminous coals were less than half that of the moisture equilibrated subbituminous coal samples investigated. Although most of the coal samples showed an increase in peroxides on drying, the high volatile bituminous coals tend to go through a maximum and then decrease, whereas the subbituminous coals go through a minimum and then increase in peroxide content.

One high volatile bituminous and two subbituminous coals were selected for studies on changes of porosity and surface area with drying. When the high volatile bituminous coal was dried, its macropore volume and surface area decreased, while the mesopore volume and surface area increased. Both subbituminous coals showed increases in macropore and mesopore volumes and surface areas on drying. Dried coal samples treated with 60% R.H. air, showed increases in macropore and mesopore volumes, and the effects were greater, the drier the coal samples. The coal with the highest equilibrium moisture content showed the greatest changes in pore volume and surface area when compared to percent residual equilibrium moisture.

The three samples used for porosity studies were also used for free radical studies. The high volatile bituminous coal showed a higher spin concentration and lower g-value than either of the two subbituminous coals. On drying, all the coal samples showed an increase in free radical concentration. The high volatile bituminous coal and one of the subbituminous coals also showed a steady increase in g-values on drying, but the second subbituminous sample showed first a decrease, then an increase. When these samples were treated with 60% R.H. air, similar effects were seen in that the free radical concentrations increased with drying, as did the

g-values, except for the second subbituminous coal. In this case, a steady decrease in g-value was observed. This latter behavior has been explained by others, and is an artifact. The increase in free radicals and shift to higher g-values indicates a change to more reactive radicals, probably on oxygen. This is borne out by the analysis of a series of Argand diagrams generated from the EPR data and fit well with the other observed data.

In summation, all parameters investigated suggest that drying coals beyond a certain minimal level increases their sensitivity to spontaneous combustion. Increases in peroxide content, free radical content, with the free radicals on oxygen, and increased pore volume and surface area are all factors which suggest that the coal becomes more reactive as it is dried. Although the thermal response analysis shows a clear relationship between residual moisture and tendency towards spontaneous combustion, the other parameters all show general trends which indicate increased susceptibility.

Further studies should concentrate on field treated samples as being more representative of the coals which are problematic to the industry. Studies should also be carried out at temperatures between 70° and 100°C so that breakdown and decomposition of peroxides and carboxylic acids can be observed. Experiments at room temperature are still in the realm of absorption phenomena and more information is needed in the regime where chemical reactions related to oxidation start to occur. This regime is reported to be in the temperature range of 70°C and above.

RÉSUMÉ

Ce projet a été exécuté sous les auspices des Laboratoires de recherche sur le charbon du CANMET pour étudier l'influence du séchage des charbons de l'Ouest canadien sur leur susceptibilité à la combustion spontanée. Ces effets ont été étudiés en mesurant la réponse thermique des charbons séchés à un traitement à l'air humide, ainsi qu'en faisant des mesures de changement de porosité et de surface, de teneur en peroxydes et de teneur en radicaux libres. De plus, une mise à jour de la recension de la combustion spontanée du charbon a été achevée, qui met l'accent sur les paramètres ci-dessus.

Six charbons de l'Alberta ont été choisis pour cette étude. Ils comprenaient trois charbons des piedmonts du rang des bitumineux très volatils, et trois charbons des prairies du rang des sous-bitumineux. Tous les charbons ont été soumis à des analyses pétrographiques, élémentaires et immédiates ainsi qu'à des analyses d'oligo-métaux. La teneur en humidité des charbons bitumineux très volatils allait de sept à douze pour cent, alors que celle des charbons sous-bitumineux allait de dix-huit à vingt-cinq pour cent. La teneur en oxygène des charbons secs sans cendre allait généralement avec le rang, les charbons bitumineux très volatils en ayant moins que les charbons sous-bitumineux.

Tous les échantillons de charbon ont été broyés et tamisés. Plusieurs échantillons de chaque charbon ont ensuite été séchés pour obtenir une gamme d'échantillons présentant des teneurs en humidité décroissant de un à deux pour cent jusqu'à ce qu'une teneur en humidité inférieure à cinquante pour cent de la teneur d'équilibre ait été atteinte. Chacun de ces échantillons séchés a ensuite été soumis pendant trois heures à une circulation d'air ayant 60 p. cent d'humidité relative, dans un calorimètre adiabatique, pendant que sa réponse thermique était enregistrée. À une exception près, tous les charbons montraient une réponse thermique négative quand ils avaient encore une teneur en humidité comprise entre soixante-dix et quatre-vingt pour cent de la teneur d'équilibre. À une teneur inférieure à soixante-dix pour cent de la teneur d'équilibre, tous les échantillons montraient une réponse thermique positive. Les trois charbons

bitumineux très volatils montraient des élévations de température qui se ressemblaient beaucoup quand la teneur en humidité diminuait, alors que les charbons sous-bitumineux montraient une réponse thermique très variable.

La teneur en peroxydes des charbons bitumineux très volatils avec une teneur d'équilibre en humidité était moins de la moitié de celle des charbons sous-bitumineux étudiés avec une teneur d'équilibre en humidité. Bien que la plupart des échantillons de charbon aient montré au séchage une augmentation de la teneur en peroxydes, celle-ci avait tendance à passer par un maximum puis à décroître dans le cas des charbons bitumineux très volatils, tandis qu'elle passait par un minimum et augmentait ensuite dans le cas des charbons sous-bitumineux.

Un charbon bitumineux très volatil et deux sous-bitumineux ont été sélectionnés pour des études sur les changements de porosité et de surface lors du séchage. Quand le charbon bitumineux très volatil était séché, le volume et la surface de ses macropores diminuaient, tandis que le volume et la surface de ses mésopores augmentaient. Les charbons sous-bitumineux montraient tous deux des augmentations de volume et de surface des macropores et des mésopores lors du séchage. Les échantillons de charbon séchés et traités avec l'air à 60 p. cent d'humidité relative, montraient des augmentations de volume des macropores et des mésopores; en outre, plus les échantillons étaient secs, plus l'effet était prononcé. Le charbon avec la plus haute teneur d'équilibre en humidité montrait les plus grands changements de volume et de surface des pores, comparé au pourcentage résiduel de l'humidité d'équilibre.

Les trois échantillons utilisés pour les études de porosité ont aussi servi pour les études sur les radicaux libres. Le charbon bitumineux très volatil montrait une plus grande concentration de spin et un coefficient G plus faible que l'un ou l'autre des deux charbons sous-bitumineux. Au séchage, tous les échantillons de charbon montraient une augmentation de la concentration de radicaux libres. Le charbon bitumineux très volatil et un des charbons sous-bitumineux montraient aussi une augmentation constante du coefficient G pendant le séchage, mais le second échantillon sous-

bitumineux montrait une diminution avant l'augmentation. Quand ces échantillons étaient traités avec l'air à 60 p. cent d'humidité relative, des effets semblables étaient observés, en ce sens que la concentration de radicaux libres augmentait lors du séchage, tout comme le coefficient G, sauf pour le second charbon sous-bitumineux. Dans ce dernier cas, une diminution constante du coefficient G était observée. Ce comportement déjà expliqué par d'autres chercheurs est un artefact. L'augmentation dans les radicaux libres et dans le déplacement vers un plus grand coefficient G indique un changement vers des radicaux plus réactifs, probablement vers l'oxygène. Ceci est corroboré par une analyse d'une série de diagrammes d'Argand créée à partir de données de résonnance paramagnétique électronique, et cadre bien avec les autres données observées.

En résumé, tous les paramètres explorés suggèrent que le séchage des charbons en-dessous d'un certain niveau minimal d'humidité augmente leur susceptibilité à la combustion spontanée. Les augmentations de la teneur en peroxydes, et de celle en radicaux libres, avec les radicaux libres sur l'oxygène, ainsi que l'augmentation du volume et de la surface des pores, sont tous des facteurs qui suggèrent que le charbon devient plus réactif quand il est séché. Bien que l'analyse de la réponse thermique montre une relation nette entre l'humidité résiduelle et la tendance à la combustion spontanée, les autres paramètres montrent tous des tendances générales qui indiquent une plus grande susceptibilité.

Les études ultérieures devraient se concentrer sur des échantillons traités sur place, comme étant plus représentatifs des charbons qui causent des problèmes dans l'industrie. Des études devraient aussi être effectuées à des températures comprises entre 70 et 100°C, de sorte que la dissociation et la décomposition des peroxydes et des acides carboxyliques puissent être observées. Les expériences effectuées à la température ambiante sont toujours du domaine des phénomènes d'absorption et plus d'information est nécessaire, dans le régime où les réactions chimiques reliées à l'oxydation commencent à se produire. Selon les informations connues, ce régime se situe dans la gamme des températures supérieures à 70°C.

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INTRODUCTION

The presence in Western Canada of abundant quantities of low sulfur, low to medium rank coals, represents a good potential for sales to Eastern and overseas markets, particularly for power plants. The difficulty with most of these coals is that they show an undesirable potential to undergo low-temperature oxidation leading to spontaneous combustion. This is especially true for coals which have undergone a preliminary drying treatment before shipment.

For a number of years the problem of spontaneous combustion has been addressed both from the point of a detailed analysis of the contributing factors, and methods to prevent its occurrence. Mechanistically, at least a dozen parameters have been examined and most of them have more or less been shown to be contributing factors. A number of schemes for the cause of spontaneous combustion have been proposed, but as yet, no definitive mechanism has been conclusively demonstrated. However, it has become increasingly evident that the two most important factors are moisture and oxygen, and the phenomenon does not occur in the absence of either. A generally accepted mechanism now seems to be that oxygen is absorbed at reactive sites in the coal. Subsequent wetting then produces a heating effect causing the oxygen to react with the coal to form peroxides. When a certain minimum temperature is reached, the hydroperoxides start to break down and start an autocatalytic reaction eventually leading to spontaneous combustion. A temperature rise of only 30 degrees can cause a rate increase by a factor of 8 to 10.

For combustion to occur, there must by a certain amount of undisturbed local heat accumulation. Subsequent exothermic reactions then add to this heat until the temperature of combustion is reached. In order for this to occur it is necessary that there be a minimum disturbance of the coal

stockpile and that air currents in the pile be insufficient to carry off the heat generated by these reactions. Methods to prevent spontaneous combustion have therefore concentrated on preventing access of air and moisture to the stockpiles. This has been accomplished to some extent by compacting the stockpile, blanketing it with an inert gas, treating the coal with some chemical agent which inhibits access of air or moisture to the coal pores or treating it with antioxidants which trap the oxygen or free radicals and in essence prevent them from participating in further oxidation. Over long periods of time none of these have been completely successful.

Since the susceptibility of a particular coal to spontaneous combustion appears to be related to the extent of its drying, it would be appropriate to develop methods which can reasonably predict the limit to which a coal can be safely dried. At the same time, it is of interest to examine some of the coal properties and how they change with drying in order to determine which seem to be the most promising for further investigation during the drying process. Since there is a variety of methods by which coal may be dried industrially, the physical properties of the coal can vary widely and this can have a significant effect on a coals susceptibility to spontaneous combustion.

From this data, it is hoped that further insight into the causes of spontaneous combustion can be found, and that this can be used to not only predict the extent of safe drying but also suggest what methods might be most profitable to pursue in searching for more effective inhibitors of spontaneous combustion. Knowing how some of the properties change on drying, one can readily examine the effects of the various inhibitors on these properties. For example, it would be possible to see whether the inhibitors

decrease free radical or peroxide content, or possibly decrease the pore volume, thus decreasing the effective surface area with which moisture can react.

This report continues the work initiated in October, 1983 and reported in April, 1986 (1). The first part updates the review from the first report on spontaneous combustion of coal with particular emphasis on moisture and oxygen, porosity and free radical studies.

The major part of the report deals with our studies on the progressive drying of six selected Alberta coal samples, three high volatile bituminous and three subbituminous, and their adiabatic response to the passage of a controlled humidity flowing gas. Changes in porosity, free radicals and peroxides were measured on samples to examine the effect of this drying and subsequent moist air treatment to see if any correlation could be made between these parameters.

LITERATURE REVIEW

There has been a considerable amount of activity in the investigation of the spontaneous combustion of coal since our last report. During this period we have continued to monitor world-wide reports in all areas of this problem. An entire session at the 1985 International Conference on Coal Science in Sydney, Australia, was dedicated to this problem and we presented a paper on the subject at the 1987 International Conference on Coal Science in Maastricht, the Netherlands (2). From the papers presented dealing with spontaneous combustion, it was obvious that the problem has universal interest. Several papers in this area were submitted by Australians. Since many Australian coals are similar to those of Western Canada, they suffer from the same commercial problem with regard to spontaneous combustion.

One contributing factor to the sudden rash of work on coal is probably the continual upgrading of instrumental techniques and the development of new technologies which allow us to probe more deeply into the chemistry of this complex material. The major driving force behind this research, however, is probably the increasing necessity for shipping and storing dried low rank coals. Another important factor is the significant investment into underground mining equipment which could be lost in an underground fire.

This review will concentrate on three areas:

I. The interaction of oxygen and moisture with coal.

II. The study of free radicals and auto-ignition of coals.

III. The changes in porosity and surface area of coals on drying and low temperature oxidation.

I. The Interaction of Oxygen and Moisture with Coal

Methods for measuring heat evolution on wetting and self heating temperatures of coal continue to appear in the literature. The self heating temperatures (SHT) of a number of coals were measured by Smith and Lazzara (3,4) using an adiabatic oven technique. They found that SHT decreased with decreasing rank and particle size. The highest risk and lowest self-heating temperatures were found when moist air was used as the test gas. The SHT was also found to be strongly dependent on the dry-ash free oxygen content of the coals.

Measurements of total heat of wetting were made by an immersion technique on oxidized Virginia-C coal. This work carried out by Phillips et al (5) involved the immersion of a coal sample in water before and after heating in air for 24 hours at 125-320°C. It was found that a 50-fold increase in the heat of immersion occurred. Oxygen content increased in the samples as the temperature increased above 150°C and a linear relationship was found between the oxygen to carbon ratio and the heat of immersion. This was attributed directly to the formation of surface carbon-oxygen bonds.

Other groups have suggested that oxidation or oxygen content of the coal tends to increase the susceptibility to spontaneous combustion. It has been demonstrated that the susceptibility of a series of Indian coals toward spontaneous combustion increases as the number of oxygen-containing functional groups increases (6).

A study on coals ranging from anthracite to subbituminous in their consumption of oxygen and rates of heat liberation on oxidation was carried out in the temperature range of 20-170°C. The Elovitch equation fit the data after a correction was made to allow for heat generation at a steady state

(7). The consumption of oxygen at a given temperature is proportional to the product of the internal surface area and the oxygen content of the coal. This suggested to these authors that oxygen-containing surface groups are acting as reactive sites. The heat evolved per mole of oxygen at the steady state was determined to be 75-90 Kcal per mole.

Heat generation from the reaction of oxygen with coal under storage conditions at low partial pressures has been studied (8.9). It was reported that an unequivocal relationship could be established between pressures of oxygen at low concentration (0-20%) and the heat generated. This agreed well with observations made at higher oxygen concentrations (10-100%). Long term experiments carried out at 32° and 50° showed losses in caloric values and in the activity of the coal. Addition of chemicals such as sulfuric acid or or iron salts, occasionally produced from aging in coal piles tend to stimulate heat generation.

An investigation using an adiabatic calorimeter with a flowing moist phase demonstrated that an equilibrium is set up between the gas phase and the solid phase and lead to an adiabatic saturation temperature. This temperature is dependent on flow rate and seems to be between 75° and 90°C under normal storage conditions. This temperature appears to be an equilibrium temperature resulting from heating by chemical oxidation and cooling by evaporation.

A Belgian worker has reported work on the exothermic absorbtion of oxygen on pulverized coal leading to self-heating and ignition (10). He has indicated that the danger increases as the content of volatiles increases and the particle size decreases. Surprisingly, he also reports that self-ignition does not occur when the concentration of oxygen in the head-gas

cloud is less than 16.2%. This does not agree with the results of other workers who report that self-ignition can occur at oxygen concentrations well below this concentration. His suggestion to inhibit auto-ignition is one which is already in practice, i.e. to inject an inert gas into the pulverized coal stockpile.

Another paper involving volatiles as a possible problem is that of Harker and Mellor (11). They report that the ignition temperature of coal decreases with increased volatile content and increases with carbon content. This applies particularly to coals with volatiles exceeding 20%. They also report that a decrease in particle size increases the susceptibility to auto-ignition.

One author (12) regards the coal particle as a semiporous body and suggests that the main parameter in the differing behavior of coals is the total surface or porosity. Moisture, a high content of fine particles and freshly opened grain surfaces promote heating. From this he deduces that the best protection from spontaneous combustion in stockpiles is compaction or covering.

A laboratory study on long term oxidation at low temperature (50°) indicated that little or no development of carboxylic acids occurs on the surface of the treated coal (13). These results were compared to naturally oxidized coal piles with the same results. The oxidized samples were analyzed by gas desorption, acid measurements, Photoacoustic FTIR and NMR.

Oxidation studies at slightly higher temperature in an in-situ FTIR system were carried out on samples of Illinois #6 (hvC) and Rawhide (SbbC) coals (14,15). These coals were thermally pretreated by heating in vacuo at 100°C and subsequently oxidized at 100°C with oxygen. Significant spectral

changes were observed. Vacuum drying at 100°C resulted in the decomposition of carboxylic acids to form a new variety of carbonyl species with Rawhide coal and decarboxylation and decarbonylation with Illinois #6 coal. Oxidation of predried Illinois #6 coal lead to the formation of new carbonyl species. The assumption that drying does not alter the chemical composition of coal is probably not correct. Overall spectroscopic and chemical changes observed in moderate temperature reaction studies may depend upon sample pretreatment, drying and storage.

A more detailed study of the structural changes during controlled low temperature aerial oxidation of an Australian high volatile bituminous coal was carried out by Anderson and Jones (16). Samples were oxidized at 50° and 100° for extended times and examined by transmission infrared spectroscopy and other techniques. Samples oxidized at both temperatures showed the same characteristic changes. Loss of aliphatic material, as indicated by changes in the infrared of the C-H region, is nonpreferential and certain aromatics such as anthracenes and phenanthrenes are oxidized even at these low temperatures. An increase in oxygen-containing compounds is also observed. The results were interpreted in terms of the chemical sites at which initial oxidation occurs, and two general mechanistic pathways were suggested. One of these involved free radical oxidation at benzylic carbon atoms followed by oxidative cleavage. The second suggests quinonoid oxidation of phenanthrene and anthracene moieties followed by cleavage to dicarboxylic acids. This is also a free radical oxidation.

Another report has appeared on the stepwise oxidation sequence of low temperature oxidation of coals (17). This author states that the thermal oxidation of coals consists of a three step sequence, all of which occur in

the range of 25 to 110°C. Two of these reactions involve oxygen directly, while the third is a thermal decarboxylation that occurs in the absence of oxygen. Oxidation at 100°C results in the formation of oxygenated species, principally carbonyl in nature, which arise from the decomposition of hydroperoxides formed at lower temperatures. Surface oxidation was found to occur even at 25°C.

A number of papers dealing with the kinetics of coal oxidation and model studies have appeared during the last three years. A Japanese group reported the kinetic study of oxygen consumption by powdered coal in the temperature range 80 to 350°C (18). The reaction appears to follow the Arrhenius equation through this region even though there appear to be three distinct steps. They are loss of moisture up too 100°, oxidation of solid organic matter up to 310° and devolatilization above 310°.

A second kinetic study attempted to relate oxidation rate to particle size (19). It was reported that the oxidation kinetics of powdered coal in air or oxygen enriched-air (87-99%) at 30-70°C depend on the coal particle size. For particles 0.233-0.718 mm in diameter, the oxidation does not depend on the initial oxygen concentration and the rate (r) is particle surface (s) controlled ($r = s^{0.3}$). For particles 1.016-4.76 mm in diameter, r is oxygen diffusion controlled. The Arrhenius activation energy is 15-20 Kcal/mole.

In a study on the maximum absorption of oxygen versus moisture content in the temperature range 60 to 90°C, it was reported that coal has its maximum absorption capacity for oxygen when it contains 40 to 50% of its equilibrium moisture content (20). This suggested to these authors that there is an optimum moisture content in coal at which spontaneous combustion is

greatest. It also suggests that it is not necessarily the driest coal which is most susceptible to spontaneous combustion. This suggestion and finding is in sharp contrast to the work of a number of other investigators including ourselves.

These authors also developed a mathematical model to calculate the moist coal-oxygen interaction. They also suggest that when the adsorbed coal-moisture bond breaks, the freshly exposed coal surface becomes active toward oxidation.

In an interesting experiment, a group of Japanese workers devised a theoretical model to determine whether exothermic adsorption of oxygen on coal is responsible for spontaneous combustion (21). A model of the adsorption was created and applied to characterize 23 coals. The model is based on the approximation that a spherical block of coal adsorbs oxygen uniformly, the heat evolved is transferred into the block solely through conduction and the temperature of the block surface is constant. The model leads to an equation for evaluating the temperature and function of time and location.

On average, when the block is exposed to oxygen at an initial external temperature of 45°C, the temperature at the block centre reaches 47.7° in 30 minutes. Once it has reached this temperature it takes approximately 100 hours for the block center to drop by 1° if the external oxygen is removed. A calculation according to a procedure in which the external block temperature is elevated stepwise to match the internal temperature as the exothermic adsorption proceeds, led to the result that the center temperature of a 100 cm spherical block may rise to 100° in approximately 16.7 hours. This rise is followed by an accelerated increase in temperature. This result indicated the possibility that low temperature oxidation of coal could cause spontane-

ous combustion. Unfortunately, no mention was made of any moisture conditions either of the coals or the oxygen atmosphere in these studies.

II. The Study of Free Radicals in Drying and Auto-Ignition of Coals

The presence of free radicals in coal has been recognized for many years. Since free radicals are known to be reactive species and are usually associated with reactions with oxygen, coal appears to be an anomaly in that coals with the highest free radical content are not the most reactive in low temperature oxidation. As coal rank increases, the free radical content increases dramatically, yet it is the low rank, low free radical content coals which are most susceptible to spontaneous combustion. The answer to this lies in the chemical structure of the coals. Low rank coals still contain a considerable portion of aliphatic carbon-hydrogen bonds, and it is the oxidation of these bonds which creates the heat necessary to set off spontaneous combustion.

Because coal is such a complex system, it is virtually impossible to resolve individual free radical signals in Electron Paramagnetic Resonance (EPR) measurements. As a result, most measurements give only spin concentration, proportional to the number of free radicals, and an average g-value which is indicative of the type of radical being measured. More recently, mathematical manipulations have allowed workers to examine changes in the nature of the radicals, but the interpretation of these changes is not yet well understood because of the complexity of the coal molecules.

In spite of these shortcomings, EPR measurements are being used to evaluate the potentiality of spontaneous combustion of coals. A number of the more recent papers on this subject are discussed here.

An interesting study on anthracite coal in a mining operation by examining the paramagnetic centers has been reported (22). These workers followed the macroscopic structure of the coal as an outburst prone area was approached. They found that as this area is approached, the paramagnetic centers in the coal increased. They concluded that this increase was not due to any change in macerals, but was probably due to mechanochemical degradation of the coal as a result of tectonic forces over a geological time period.

A laboratory examination of two low volatile bituminous coals by ESR and electron spin echo (ESE) techniques has been carried out (23). Two natural and heat-treated coals were examined. In all samples, two main paramagnetic centers were detected and studied selectively by observing the ESE decays at different parts of the ESR signal. These centers interact differently with neighboring protons and the interaction is reduced in both centers by heat treatment. The ESR measurements reflect the heterogeneity of the region around the radical and are sensitive to the presence of proton hyperfine and dipolar broadening interactions.

The interaction of a brown coal with air at 25°C and 75% relative humidity showed a tendency to an overall decrease in paramagnetic centers (24). However, over a period of 230 days, the paramagnetic centers concentration vs. time plots showed a typical EPR spectrum with 5-6 maxima and minima. This suggested to the authors that fresh coal has a metastable chemical structure which in open air storage undergoes several structural changes, some of which may cause self-ignition.

It has been suggested that the atmospheric oxidation of an Australian high volatile bituminous coal (Blair Athol) proceeds through a typical radical mechanism, leading to the emission of hydrocarbon gases and the formation

of anhydrides and carbonyl functions (25). The initial rapid uptake of oxygen indicates a large number of reactive sites in the coal structure that readily react with oxygen.

A profile of the change in free radical concentration of two U.S. coals under pyrolytic and oxidative treatment was followed by ESR (26). Illinois #6 and Montour coals were heated in the presence of oxygen from 140°-400°C. Free radical concentrations were plotted as a function of time of treatment at a given temperature. Initial increases in the organic free radicals were observed at all temperatures, but at the higher temperatures, termination reactions caused the increase to be transient. Variations in the free-radical concentrations of weathered and unweathered coals showed that the former produced a larger number of radicals. It was suggested that some of these effects may be due to native mineral matter.

The effect of drying on the reactivity of a Victorian brown coal was followed by its free radical content (27). It was found that a coal sample when dried at 35° or 55° in a vacuum had a higher free radical content than a sample of the same coal dried in a laboratory atmosphere at a temperature of 35° and 55° for six weeks followed by vacuum drying to the same moisture content as the straight vacuum dried coal. Examination of the reactivity of these dried coal samples to a pure oxygen atmosphere showed that the straight vacuum dried coals were more reactive than the air dried vacuum dried coals of the same moisture content. This suggests a lower sensitivity to spontaneous combustion for air dried coals. Mathematical models were derived which describe the number of active coal sites, equated as numbers of free radicals as exponential and linear functions of temperature. In another set of experiments on drying of coals versus free radical content, a Wyoming subbituminous coal of 50% moisture content and an Australian brown coal

(Morell) of 59% moisture were used (28). Weight loss on drying at 110°C was correlated with changes in radical concentration, g-factor, linewidth of NMR, IR and elemental analysis. Both coals exhibited a substantial increase in radical concentration on drying at temperatures from 20 to 150°. Elemental analyses showed that the Wyoming coal lost water and CO_2 on extended drying. The loss of CO_2 was substantiated by IR spectroscopy.

III. The Changes in Porosity and Surface Area of Coals on Drying and Low-Temperature Oxidation

In any study on the surface oxidation of coal, porosity and surface area must be an important part of that study. Since this reaction is heterogenous, the potential reactivity of the coal with oxygen is directly proportional to its surface area. Porosity, on the other hand, determines how much oxygen can reach that surface. One thinks of oxygen as a small molecule, but many of the pores in coal, the so-called micropores, are of small molecular dimensions, and it is not difficult to recognize that it is possible for those pores to be blocked by condensed or adsorbed molecules such as water or the volatiles found in coals.

It has been only recently that workers have started to try and correlate the relationship of surface area and pore size with the phenomenon of spontaneous combustion by measurements taken during drying or oxidation, rather than merely hypothecating.

Parkash and Chakrabartty have studied the porosities of 11 Alberta Plains coals (29). Porosities were scanned by gas adsorption, helium and mercury displacement and mercury porosimetry. Surface areas calculated from CO_2 adsorption at 25° ranged from 75-506 m^2/g and were found to be much high-

er than those calculated from nitrogen adsorption at -196°, which were found to be 1-9 m^2/g. Samples from the Paskapoo deposits were found to have slightly higher surface areas than those from Horseshoe Canyon deposits.

The carbon content of the coals tested ranged from 73.4 to 76.8% and is too narrow to allow for calculating the influence of this parameter on porosity or surface area. Total pore volumes are measured in the range 1.2 to 3000 mm and are divided into three groups: micropores (< 1.2 mm), transitional pores (1.2-30 mm) and macropores (30-3000 mm). Most of the surface in coal is in the micropores. Coals vary widely in their total pore volumes and porosities range between 9.5 and 22.3%. The percent pore volume contained in the macropores ranges between 18.5 and 50%, in the transitional pores between 1.1 and 20.5% and in the micropores between 29.5 and 75.9%.

Investigation of the changes in porosities of two Spanish coals with heating have been reported (30). A semi-anthracite coal and a high-volatile bituminous coal were subjected to a heat treatment and the change in porosities measured. Nitrogen and CO_2 adsorption isotherms and mercury porosimetry indicated that the semianthracite was more microporous than the bituminous coal. On heating, the bituminous coal showed a substantial increase in both the macropores and micropores, while in the semi-anthracite the macropores increased and the micropores decreased. The microporosity was unaffected in either coal when subjected to an acid demineralization, but the macroporosity increased.

The moisture retention capacity of coals ranging from lignite to anthracite has been measured and its relation to oxygen content and pore structure was investigated (31). Both factors play a role in the water-holding capacity of a coal.

CONCLUSION

Most of the work presented in this review has tended to solidify our present concepts of spontaneous combustion, and the overall sequence occurring during spontaneous combustion seems to be reasonably clear. There are still gaps in our knowledge of what might be a triggering mechanism for this phenomenon.

More sophisticated model studies have appeared and more emphasis seems to be appearing about the physical and chemical changes on drying and heating coals, in particular in the areas of porosity and free radicals. There has been very little emphasis on either trace metals or macerals in the past few years.

Although it is still of importance to discover the complete picture of what causes spontaneous combustion, it is now time to put more emphasis on methods to predict the susceptibility of a coal toward spontaneous combustion, and to find methods to inhibit this hazard in commercially dried coals. We look to the future for more work in this area.

EXPERIMENTAL

I. Collection of coal samples

Three samples of high volatile bituminous coals were collected from Alberta foothills mines and three subbituminous coals were collected from Alberta plains mines. One of the high volatile bituminous coals was selected especially for its high exinite content. Personnel from the Coal Research Laboratory, Calgary, CANMET, assisted in the collection of the coal samples.

II. Sample preparation

Coal samples were crushed and sieved to a mesh size of -60 to +200. All operations were carried out under an atmosphere of argon to prevent oxidation. Samples were stored later in glass bottles under an argon atmosphere.

Samples were initially equilibrated at a relative humidity of 97% and then progressively dried over P_2O_5 in a vacuum desiccator. Residual moisture was determined by carrying out loss on drying on an aliquot of a representative sample at 105°C for one hour.

III. General coal properties

Petrographic, proximate, ultimate and mineral analyses were carried out on all coal samples.

Petrographic analyses were carried out by Dr. Alex Cameron at the Institute for Sedimentary and Petroleum Geology and are reported in Table 2. Proximate analyses were carried out at Loring Laboratories Ltd. Calgary and these results are reported in Table 3.

Ultimate analyses were carried out at the Department of Chemistry and

the Kananaskis Center for Environmental Science, The University of Calgary. These analyses are listed in Table 4.

Metal contents were determined by Inductively Coupled Plasa Analysis (ICPA) by Metro Tech Systems Ltd. of Calgary and are reported in Table 5.

IV. Adiabatic Calorimetry tests

The adiabatic calorimeter used in these experiments was described in the first report (1), except that a cold water circulating system has been added so that subambient responses can also be accommodated. The prepared samples (25 g) were placed in the reaction vessel of the adiabatic calorimeter and the starting temperature was set on the control panel. Dry oxygen-free nitrogen was pass through the sample at a rate of 20 ml per minute until temperature equilibrium had been reached. When equilibrium had been reached the flowing gas was changed to 60% R.H. Air at a flow rate of 150 ml per minute and the thermal response was measured for three hours. The bath temperature was kept equilibrated with the coal by a feedback mechanism whereby the bath could be either cooled or heated to keep it at the same temperature as the coal. The temperature of the coal was measured by a thermocouple placed in the middle of the coal sample and was recorded continuously over the entire range of the experiments.

V. Peroxygen analysis

The peroxide content in the coal samples was determined by the titrimetric method used in our previous report (1). This method involves treating the coals with a ferrous ammonium sulfate solution which reacts with the peroxides to produce ferric ions. After 15 minutes, the ferrice ion is

titrated with a standard solution of mercurous nitrate containing excess ammonium thiocyanate. With every set of peroxide analyses carried out, a black was run simultaneously.

VI. Porosity measurements

Pore volumes and surface area were measured using a Quantachrome Autoscan 60 mercury intrusion porosimeter with 0.5 cm^3 capacity cell. Por volumes were measured down to 18 A radius.

VII. Free radicals

Free radical concentrations and g-factors were determined by Electron Paramagnetic Resonance (EPR) using a quartz tube (3 mm i.d. and 4 mm o.d.) in a 9 GHz (synchrodyne) spectrometer with a 400 hz magnetic field modulation and a T_{011} cylindrical cavity.

RESULTS AND DISCUSSION

I. Progressively Dried Coal Samples Treated With 60% R.H. Air

With the modification of our adiabatic apparatus, subambient heat effects have become more realizable. A relative humidity of 60% was chosen for our adiabatic experiments as being the most representative for natural conditions in Alberta. The results would therefore represent more realistically the responses of coals in Alberta to a natural environment. The results of passing 60% relative humidity air over our six samples of coal which have been progressively dried to less than 50% of their saturation moisture content are shown in tables 6-11 and Figures 1-6. Coal samples were dried to provide samples representing small incremental decreases in moisture. This was carried out until a moisture content less than 50% of the equilibrium moisture content had been reached.

The data show that the responses to this treatment are fairly readily segregated by coal rank, although the subbituminous coals are somewhat more erratic in their results and subbituminous coal D tends to look like a high volatile bituminous coal. It is interesting to note that the H/C ratio of coal D is more like that of the high volatile bituminous coals than the subbituminous samples (see Table 4). All of the coals show subambient responses when they are at equilibrium moisture content, and several even on partial drying, although this tends to be the case more with the subbituminous coals which have a much higher equilibrium moisture content. Since this thermal response is a combination of cooling by desorption, heating by adsorption and possible oxidative reactions plus other reactions of unknown nature, it is difficult to predict at what point a positive thermal response will occur. It is certainly related to the moisture content of the coal and the relative

humidity of the flowing gas. In particular, it must be related to the equilibrum moisture content of a particular coal at a particular relative humidity and this data does not seem to be available.

Five to six samples of each high volatile bituminous coal (samples A-C) were examined with moisture contents ranging from 100% to 30% residual moisture. On examination of these three coals, one sees that the temperature responses are all very similar. These coals range from moisture content of 7.5% to 11.9%, and in Figures 1-3 these differences are normalized by plotting the amount of heat evolved for each experiment in terms of the percentage of the saturated moisture content of each coal. The heat evolved was calculated from the heat capacities of the individual components of each coal sample based on its water content and proximate analysis.

In a composite plot of percent residual moisture versus heat evolved, Figure 7 shows that from approximately 70% residual moisture down to the limit of our experiments (approx. 30% residual moisture) the amount of heat generated is almost directly proportional to the extent of drying. In other words, in this region of the response curve, the response is roughly linear. This suggests that, at least for this series of coals, the extent of drying in percent of residual moisture rather than the absolute residual moisture is important, a result which we have observed before (1).

One coal, sample C, shows an initial rise and then fall in the response curve when approximately 10% of the equilibrium moisture has been removed by drying. This experiment is reproducable and the phenomenon also occurs with one of the subbituminous coals examined. We have no explanation for this apparent abnormality at this time.

The three subbituminous coals tested (D-F) had equilibrium moisture contents which ranged from 18.4% to 24.6%. Six to eight samples of each of these coals were examined with residual moisture contents ranging from 100% to 11%. These coals showed a high degree of variability in their response to the adiabatic moist air treatment. Coals D and F were similar in their responses, as can be seen in Tables 9 and 11 and Figures 4 and 6 with cooling tendencies up to about 70% residual moisture content and then a steady climb as the moisture content was decreased. Coal D closely resembled the high volatile bituminous coals between 70% and 35% residual moisture as can be seen in the composite Figure 8. Coal F, however, shows a smaller thermal response in this region and only begins to evolve considerable heat after its moisture content has been reduced below 30% residual moisture. Coal E is anomalous. At high residual moisture content it resembles a high volatile bituminous coal in that it shows little subambient response, but on reducing the residual moisture to less than 60%, it shows a very sharp thermal response, and with residual moisture content of less than 50% the amount of heat evolved was well above any of the other coals examined (see Table 10, Figure 5).

A word of caution should be made here when attempting to extrapolate these results to commercial coal drying processes. These processes generally involve heating the crushed coal to temperatures exceeding 100°C. At these temperatures many reactions occur in the coal which is not expected with samples which have been dried at approximately 20°C in a vacuum. The commercial drying methods use considerably higher temperatures, thereby decomposing peroxides and carboxylic acids. As a result, the coal surface may become more reactive compared to coal samples dried at room temperature.

II. Peroxygen Content in Coals

Initial peroxygen contents in the coals were found to be roughly related to the equilibrium moisture content or rank of the coals. Peroxygen counts on the high volatile bituminous coals A-C ranged from 25% to 50% of the subbituminous coals D-F which were analyzed. Examination of the peroxygen content of the coals on progressive drying did not give consistent results. These results are reported in Tables 12-17. Coal sample A, a high volatile bituminous coal, showed a gradual rise in peroxygen content to a value greater by 78% as the moisture content was decreased to 45%. Coal sample B, also a high volatile bituminous coal, showed an increase up to a maximum of 81% but decreased to 23% after the sample was dried to 35% residual moisture. The third high volatile bituminous coal (sample C) decreased to a minimum of 82% of the initial peroxygen content, then rose to a value 36% higher as it was dried to 30% residual moisture. Coal C also showed anomalous heating behavior during adiabatic studies so long as it contained a high percentage of its residual moisture. It is assumed that this is indicative of the breakdown of the peroxides, but this is only a conjecture.

It was difficult to correlate peroxygen content with progressive drying of subbituminous coals. Coal samples D and F both showed a gradual increase with drying to peroxygen values 91% and 49% greater than the initial peroxygen content respectively. These final values were for samples dried to approximately 39% residual moisture. However, both of these samples showed a decrease of peroxygen content at an intermediate moisture content. The third subbituminous coal, sample F, showed a gradual decrease in peroxygen content to a minium of 53% of the initial value at a residual moisture content of 59%, then a gradual increase to 76% at 40% residual moisture content and finally to 96% of the original peroxygen content at 11% residual moisture.

When these coal samples were treated with moist air of 60% relative humidity in adiabatic studies, the changes in the peroxygen content in most cases were so small as to be within experimental error. They followed the same rise and fall patterns as the dried samples did, so it can be postulated that the flowing gas had little effect on the peroxygen content on dried coals. These results are not completely unexpected since the temperature rises have been very small in these experiments, the highest rise being only a change of thirteen degrees. The reaction of oxygen with coal at or near room temperature to form peroxides is a fairly slow reaction, adsorption being the main interreaction. As the temperature rises, the oxidation reaction is accelerated by roughly a factor of two for every ten degree rise. So a rate factor of only roughly two would be expected in our most extreme case here. In our previous work we were experiencing temperature rises of 20° to 30° and a rate factor of 8 is sufficient to be able to see significant changes in these reactions.

Commercial drying will obviously have a very decided effect on peroxygen content since at 100° a rate factor of peroxygen decomposition of about two hundred and fifty is predicted, and many of the initial peroxides will have decomposed during the drying process. However, during cooling, the coal will be exposed to air and the formation of peroxides will again occur.

III. Porosity and Surface Area of Selected Coal Samples

Because of time and instrument constraints, only one high volatile bituminous coal (sample C) and two subbituminous coals (samples D and F) were selected for porosity and surface area studies. These coals were selected as representative of the two ranks being studied and the high volatile

bituminous coal C showed only a small effect on the macropores (>30 Å) and a slight volume decrease and area change was noted as the coal was dried from saturated moisture content (11.91%) to 30% of its equilibrium moisture. However, the mesopores (30-18 Å) showed an increase. Both the mesopore volume and surface area increased by 24% over this drying range.

When the moisture saturated and partially dried samples of C were treated with moist (60% R.H.) air, the moisture saturated sample showed a sharp decrease in the macropore volume and surface area, but a small increase in the mesopore volume and area. On examining the moisture treated progressively dried samples, it was found that the macropore volume and area steadily increased to values greater than the untreated coals, whereas the mesopores showed first a decrease and then an increase to slightly above the untreated coal samples. These results can be seen in Table 18 and Figure 9.

In both subbituminous samples D and F the macropore volume and associated surface area increased on drying. Treating the moisture saturated and progressively dried samples of coals D and F with moist (60% R.H.) air increased the macropore volume and area and these values increased as the samples were progressively dried. These two coal samples acted differently with respect to their mesopores. With dried but untreated samples, coal D showed an initial decrease in mesopore volume and area but then increased to values above those of the equilibrated sample. On the other hand, coal F showed a steady increase through all steps of drying. When these two coals were treated with the moist air they both showed a decrease in the mesopore volume and area with the moisture equilibrated samples, but then showed a steady rise to reach values which were still slightly below those of the untreated samples of the same dryness. These results can be seen in Tables 19 and 20 and Figures 10 and 11.

With the exception of the macropores of the high volatile bituminous coal, the general trend seems to be that, on drying, the pore volumes and surface areas of these three samples increase. This means that there is increased exposure of surface area for attack by atmospheric oxygen, and an increase in the potential for spontaneous combustion. Under the conditions of the adiabatic moist air experiments there does not appear to be a significant difference in the pore volumes or surface areas of any of these three coals when comparing them to the typical dried coal samples. Again we are dealing with only small temperature rises in these experiments.

All three of these coal samples have similar pore volumes and surface areas with coal F having values about 15% less than coals C and D. On drying these samples to about 30% residual moisture, samples C and D showed surface area increases of 10 to 37%, sample F showed increases of 52 to 63%. Coals C and D therefore appear to be very similar in their responses to drying and moist air treatment with the subbituminous coal D show slightly greater overall increase in pore volume and surface area than the high volatile bituminous coal C. However, the high moisture content subbituminous coal F shows the greatest changes and these are from the lowest pore volume and surface area in the saturated samples to the highest pore volume and surface area in the dried samples. Since this represents the greatest increase in surface area, one would predict that this coal should be the most susceptible to spontaneous combustion if surface area within a coal rank is an important factor.

IV. Free Radical Analysis of Selected Coals

Free radical studies were carried out with the same coals (C, D and F) selected for porosity studies. Although it is impossible to resolve the ESR

spectra into individual radicals, it is possible to get some useful information from them by mathematical manipulation. A comparision of the number of radicals can be obtained directly by area counts, and a g-value, which is characteristic of the types of radicals in the coal, gives some idea as to the sites of the radicals. The g-value is only the average of all the radicals present. Computer resolution of the ESR spectrum in terms of Gaussian versus Lorentzian shape and half height width can be used to produce any one of a number of Argand diagrams. This so-called DISPA analysis produces dispersion diagrams which indicates changes in the types of radicals present. As yet, it is not possible to interpret the meaning of these changes. Generally speaking, it has been accepted that as g-values increase, the radicals tend to be more on hetero-atoms rather than on carbon, but it is not possible by these techniques to distinguish between different types of carbon radicals.

The data for the ESR spectra of the coals analyzed appear in Tables 21-23. The corresponding Argand diagrams are seen in Figures 12-14. All samples of coals, whether from progressive drying alone or progressive drying followed by treatment with moist (60% R.H.) air showed increases in radical content with drying. The g-values of the high volatile bituminous coal C and subbituminous coal F also showed increases in drying, but subbituminous coal D was different. This showed a decrease in g when the moisture content was reduced by 60% equilibrium moisture, but it then increased to slightly higher than the moisture equilibrated sample by the time it had reached 38% equilibrium moisture. Moisture equilibrated sample D, when treated with 60% R.H. moist air, reached a g-value well above that of the untreated sample, but treatment of successively dried samples in the same manner gave a steady decrease in g-value to well below that of the moisture equilibrated sample.

The Argand diagrams used in the analyses for all coal samples show two negative radial difference peaks at approximately 120° and 240°. The relative intensities of these peaks seem to vary with g-values. When g-values are in the range of 2.00216, the 240° peak predominates. As the g-value increases, the 120° peak increases until at approximately g = 2.00235, both peaks are relatively equal. At g-values higher than this, the distortion toward an intense 120° peak occurs to the point where the 240° peak becomes only a shoulder on the curve.

Looking at Table 21 and Figure 12 for high volatile bituminous coal C, we see that on drying this coal to 56% of its equilibrium moisture the g-value changes by only a very small amount. This is reflected in the Argand diagrams (Figure 15) where one sees a negligible difference. However, when the sample is further dried to 30% residual moisture, the g-value shows a considerable increase and the relative heights of the 120° and 240° peaks change so that the 120° peak dominates. Looking now at the moist air treated samples of moisture saturated coal C and coal C dried to 56% and 30% residual moisture (Table 21 and Figure 12), the moisture equilibrated sample has the same g-value as the untreated and the Argand diagram (Figure 18) is the same. As progressive drying occurs, the g-values increase more rapidly and the swing to a highly dominant 120° occurs already at 56% residual moisture and in the 30% residual moisture sample the 240° peak is only a shoulder.

Subbituminous coal D is the only sample which showed a decrease in g-value on drying (Table 22 and Figure 13). The moisture equilibrated sample has a high g-value and the 120° peak dominates slightly (Figure 17).

On reducing the moisture to 60% of the equilibrated value the g-value drops considerably and the dominant 240° peak is now observed. On further drying to 38% of equilibrium moisture, the g-value rises above the original value and now the strongly dominant 120° peak reappears.

When samples of moisture saturated coal D and coal D dried to 60% and 38% residual moisture are treated with 60% relative humidity air, the g-value of the saturated sample increases considerably and the 120° peak strongly dominates (Figure 18). On treating the 60% moisture sample in the same manner, the g-value drops, but the diagram in this case doesn't follow and the 120° peak still dominates. However, when the 38% moisture sample is treated, the g-value drops to a low value and the two peaks are almost equal.

With the second subbituminous coal, sample F, all g-values were high (Table 23 and Figure 14). The 120° peak predominated strongly in all cases and the 240° peak was hardly more than a shoulder in most of these Argand diagrams (see Figure 19). The lack of a shift of peak intensities with drying is ascribed to the fact that this coal has a high g-value to start with and hence the dominant radicals in this coal are already present in quantity sufficient to skew the curve to the 120° peak. Increasing the drying only tends to skew it further.

Treatment of the moisture saturated coal F, as well as samples dried to 31% and 11% residual moisture with 60% moist air gave results which followed those of the dried samples closely except that the g-values and radical content did not rise as high (Table 23 and Figure 14). The Argand diagrams were also similar in that even the moisture saturated sample already showed the strongly dominant 120° peak (Figure 20).

As has been mentioned before, the absolute quantity of free radicals and the g-value are rank and moisture dependant. The higher the coal rank, the greater the concentration of free radicals. In our samples we see that sample C, a high volatile bituminous coal, has the highest spin concentration. The two subbituminous coal samples D and F show lower spin concentrations than coal C, and F, having the higher saturation moisture, has the lower spin concentration of the two.

On the other hand, with the exception of very high rank coals, g-values are lower with the higher rank coals. This has been attributed to the localization of more spins on aromatic carbon systems which approach the value of the free electron, whereas higher g-values are associated with hetero-atoms, in particular oxygen and sulfur, and which are higher as rank decreases. We can see this conclusion borne out with our samples where the high volatile bituminous coal C with an oxygen content of 14.31% has a g-value of 2.00216 whereas the subbituminous coals D and F with oxygen contents of 24.26% and 25.14% respectively have g-values of 2.00235 and 2.00238 respectively.

The increase in spin concentration and higher g-values of coals C and F on drying or on drying and treating with moist air suggest that there is an increase in oxygen radicals in these coals. The effect seems to be associated more with drying than with the moist air treatment since comparing coal samples at the same stage of dryness for the same coal, the dried sample always shows a higher spin concentration than the same coal treated with moist air. The g-values also follow this same pattern very closely. The behavior of coal D with regard to g-values is rather disturbing. Although the spin values increase with drying, the g-value decreases and then

increases in drying, but decrease steadily for coals which are treated with moist air after drying. There is an explanation for behavior of this type when a coal is dried (32). It was found that this behavior was apparently due to the electrical resistivity of the coal and was a function of the particle size. When these authors ground their sample very finely and mixed it with potassium bromide, it was found that the g-value returned to its expected value in line with other samples which did not show this anomalous behavior.

CONCLUSIONS

This project was designed to test the extent to which a number of Alberta high volatile bituminous and subbituminous coals could be safely dried. This was to be done by taking samples of each coal and preparing series of samples dried in small increments of 1 to 2% moisture content until a sample of less than 50% residual moisture content was reached. Each of these dried samples was then to be subjected to a flowing stream of moist air and the thermal response measured. Subsequently, other property changes such as peroxide content, free radicals and porosity were to be measured. It was hoped that this could be used as a test to predict the level to which a coal could be dried and still be safe to store or ship.

Three high volatile bituminous and three subbituminous coals were selected for these studies. All were subjected to the gas flow experiments, and peroxides were determined. One high volatile bituminous and two subbituminous coals were used for the porosity and free radical experiments. All coal samples were dried to various moisture levels at room temperature in vacuo and then subjected to a flowing gas of 60% relative humidity air in an adiabatic calorimeter. The value of 60% R.H. was chosen as being fairly representative of an Alberta summer atmosphere moisture.

The responses of the dried samples from the three high volatile bituminous coals were generally very similar. When the equilibrium moisture of the coal samples was 70% to 80% of equilibrium moisture or greater, the thermal response was negative, indicating that the major effect was desorption and drying by the dryer air. When the moisture of the samples was decreased below 70% to 80% equilibrium moisture, the exothermic reactions such as wetting and possibly oxidation start to take over and a positive

thermal response is seen. The temperature rise is essentially linear for all three of the hvb coal series between 70% and 40% equilibrium moisture content.

The subbituminous coal samples showed widely varying thermal responses. In general, their responses were similar to the hvb coals in that when the residual moisture content was 70% to 80% or greater of the equilibrium moisture, the thermal response was negative. When the residual moisture content was reduced to below 70% to 80%, the thermal responses varied from greater than that of the hvb coals to less than these coals.

By correlating these thermal responses in terms of susceptibility to spontaneous combustion, it would appear that there is little possible risk with drying a high volatile bituminous or subbituminous coal to approximately 75% of its equilibrium moisture content. After that its susceptibility seems to increase almost linearly with the decrease in moisture.

Peroxide content follows with rank: the lower the coal rank, the higher the peroxide content. Although the sample in this study is small, this can be seen clearly in our previous report (1) and the peroxide contents of these samples agree well with those previously examined. The response of these coal samples with respect to peroxide content on drying was extremely erratic. Coal sample A (a hvb coal) and samples D and E (subbituminous coals) all showed a gradual increase in peroxide content with drying. This increase ranged from 50% for sample E to roughly 100% for samples A and D.

Coal sample B showed an initial increase in peroxide content on drying to 70% residual moisture, but when the residual moisture content was reduced to below 70% residual moisture the peroxide content dropped. Coal samples C and F both showed initial decreases in peroxide content, on being reduced to

approximately 70% residual moisture, but with further drying, both of these samples showed increases in peroxides.

The peroxide content of dried coal samples treated with moist air followed very closely the same patterns as the dried-untreated samples. The actual peroxide contents did not change significantly in moist air treated samples from the corresponding dried-untreated samples and on the average were slightly lower than the dried-untreated samples.

Since these coal samples were dried at room temperature in vacuo, one would not expect a large change in peroxides due to thermal decomposition. Further, one would expect a slight increase due to the overall reduction in mass due to loss of water. However, simple calculations show that the peroxide content does not follow the mass loss pattern (See tables 12-17). In one case (coal F) we actually see a net loss in peroxides, and this occurs at intermediate steps in drying with several of the samples. In those cases where overall increases were observed (samples A, D, and E), the increases were far greater than the corresponding mass loss.

From these results it would appear that no significant increase in peroxide content occurs during the interaction of moist air with coal at these low temperatures, and probably the only effect is absorption of oxygen in the coal pores. This agrees with work of previous workers (33) who report that the first stage of the coal-oxygen reaction is chemisorption and that rates of oxidation below 70° are generally low.

Although porosities of coals have been measured before, no measurements seem to have been made in porosities with drying at ambient temperature. As reported in the review, some measurements have been made on heated samples, and in one case a sample was heated to 450°, but this was on a lignite.

Since porosity should be related to ability of oxygen to penetrate the coal and attack fresh surfaces, any change in the porosity should relate to thermal responses when these coals are treated with moist air. Using mercury porosivity, one can measure pore volumes down to about 18Å. This is roughly in the middle of the mesopore region which has been suggested as being between 30 and 1.2Å. Below this is the micropore region and above is the macropore region. Surface area increases as pore size decreases and pore volume increases. The smaller the pore size, the greater the pore volume, and because of this, the bulk of the surface area in a coal is in the micropores. This does not necessarily mean that oxidation will occur in the micropores, since there is the problem of these molecules getting into the micropores.

On examining the changes of porosity of a high volatile bituminous coal (Sample C) with drying, it was found that the macropore volume decreased, but the mesopore volume increased. This is presumably due to collapse of the macropores as the moisture is removed. The overall result was a net increase in surface area.

Treatment of a number of dried samples of coal C with moist air showed a sharp decrease in the macropore volume and a small increase in mesopore volume on the equilibrated sample, leading to little change in the overall surface area. As this was carried out on a number of successively dried samples, a decrease in surface area is found followed by an increase to an even larger surface area with the most highly dried sample.

With the two subbituminous coals (Samples D and F) the macropore volumes of a number of successively dried samples steadily increased on drying. This suggests that there is no collapse of these macropores on drying. The same

pattern was observed with the macropore volumes of the same successively dried samples when they were treated with moist air. A steady increase was again observed as the drier samples were examined. Changes in the mesopore volumes were somewhat erratic, but in both cases, the overall results were increases in total surface area. Both coals showed a steady increase in mesopore volume when a number of successively dried samples were treated with moist air. Coal F with the highest equilibrium moisture content almost doubled in surface area.

Free radicals are normally associated with reactivity when discussing organic molecules, but not all free radicals are capable of initiating oxidation. In fact, some organic compounds are used as oxygen scavengers since they react to form stable radicals which are incapable of abstracting a hydrogen atom from a carbon atom, the normal start of an oxidation sequence. These radicals are usually associated with aromatic systems. Coals of high rank have a high level of aromaticity and also a high concentration of free radicals. However, these radicals are of the more stable variety. As coal rank decreases, the aromaticity decreases and the concentration of free radicals decreases. However, the reactivity of these radicals increases. This is because they tend to be more on the hetero-atoms in the coal structure and most probably on oxygen atoms. This can be seen by examining the g-values of the radical spins as measured by ESR. As the rank of coal decreases, g-values get larger and this is indicative of a change from radicals on carbon to radicals on hetero-atoms.

When we examined our coal samples by ESR, we found that the subbituminous coals had higher g-values than the high volatile bituminous coal. We also found that the spin concentration, indicative of the number of

radicals, was lower in the subbituminous coals. As these coals were progressively dried, the spin concentration increased. This also occurred as the same series of progressively dried coals were treated with moist air, however the dried, untreated coal samples were always higher in spin concentration than the moist air treated samples.

Examination of the changes in g-values was more interesting. With the high volatile bituminous coal and one of the subbituminous coals, g-values increased significantly with drying, or with drying followed by treatment with moist air. These showed a pronounced tendency to a shift to radicals on hetero-atoms. This is undoubtedly a shift to radicals on oxygen. A very large shift on the one subbituminous coal (sample F) correlates well with the large pore volume generated on drying.

In contrast to this, the subbituminous coal (sample D) shows an almost opposite effect. On drying, this coal first shows a decrease in g-value and then an increase. However, the moist air treated samples show a steady decrease in g-values. This coal also showed a slight decrease in pore volume followed by an increase, but it doesn't fit the steady increase of spin concentration. An explanation for this behavior has been offered in the literature (32).

In summation, it would appear that drying of low rank coals increases the concentration of reactive free radicals, i.e., those on hetero-atoms such as oxygen. This suggests that any subsequent treatment which would activate the coal in the presence of oxygen would cause these radicals to react with the carbon-hydrogen bonds and initiate oxidation and ultimately spontaneous combustion. The most likely form of activation is, of course, heat.

All of these experiments have been carried out at or near ambient temperatures, including the drying procedures. Because of this, all of the

interactions investigated have been in the early stages of oxidation and probably only oxygen adsorption and heat of wetting are occuring. In several cases, trends are seen, but there always appear to be one or two anomalous samples in the group. In spite of this, there are indications that changes which could affect the tendency of a coal to undergo spontaneous combustion can be indicated by measurements of changes in peroxide and free radical content, as well as changes in pore volumes and surface area, and thermal response to moist air when these measurements are taken on series of progressively dried coal samples. Increased pore volumes and a buildup of a high concentration of oxygen radicals in the coal are two examples of this. These measurements would obviously be of greater value if they were made on samples dried under commercial conditions.

RECOMMENDATIONS

This project has been a continuation of our studies on the effects of drying Western Canadian coals. This was carried out primarily by examining the thermal responses of passing moist air (60% R.H.) through a number of sequentially dried samples of different coals.

The coal samples chosen were dried in small increments to get a better idea of where sudden changes in measured parameters might occur and then attempt to correlate these results with the susceptibility of a coal to spontaneous combustion. In addition to thermal response, changes in peroxide content, free radical content and porosity and surface area were measured.

The ultimate goal of this project is to establish the safe levels of drying coals for transportation or storage. All of these studies were carried out at or near room temperature (20°C) and samples were dried in vacuo at room temperature. In the future, it would be more reasonable to work with samples which have been dried under conditions similar to field samples. The drying of mined coals is generally accomplished thermally at temperatures ranging from 80° - 150°, not in vacuo at room temprature over a drying agent. The reactions which occur in a coal on heating to temperatures of 70° or above are accelerated compared to those which occur at room temperatures. This is above the critical temperature which has been accepted for low-temperature auto-oxidation to occur. As such, pore volumes, free radicals, peroxides and in particular, the interactions with moist air will show more pronounced effects than those which we have measured here.

One difficulty with this project has been that we have no actual correlation between our results and the susceptibility of the examined coal samples to spontaneous combustion. All of our data can be interpreted as

being able to contribute to spontaneous combustion in terms of the reaction mechanism which is gradually emerging from this work. However, as yet, there is no good method for a quantitative evaluation of a coal as to its susceptibility to autoignition. This is an area which still requires a great deal of research, and is necessary to evaluate the significance in the changes in the various parameters which may contribute to spontaneous combustion.

Because a serious problem exists in storing and transporting dried Western Canadian coals, it is important to examine how these parameters do change when the coals are dried thermally. Many of the Alberta coals are of medium water content, and they must be dried to achieve an acceptable BTU level, and in this condition many of these coals are highly susceptible to spontaneous combution. To date, no measurements have been made on these thermally dried coals to see how the various parameters have changed. For example, changes in porosity, free radical content, peroxide content and possibly the most revealing parameter, their susceptibility to thermal rise when treated with moist area. Although we have made measurements on samples dried at 20°, the changes in these parameters should give important data as to the susceptibility to spontaneous combustion of thermally dried coals.

After investigation of the aforementioned parameters in the commercially dried coals, steps should be taken to find inhibitors to spontaneous combustion based on the changes observed. Ideally, one should be able to treat these coals with some inexpensive agent to inhibit autooxidation, but with the exception of coating with heavy oil, no other treating agent seems to be in general use. Most of these treatments are empirical and no detailed studies have been made on the effects of the treating agents on the various

parameters contributing to spontaneous combustion. For example, it would be of interest to examine how a selected number of inhibitors of various classes affect the porosity and surface area of a commercially dried coal sample. Of equal interest would be changes of peroxide and free radical content. If the inhibitor treated coal samples were subjected to moist air flow, the thermal responses would be of great interest since these responses are a direct reflection of the reactivity of a coal sample with oxygen and moisture.

Our recommendation for future work is that emphasis be placed on commercially dried coals and the changes in its physical and chemical properties. This should then be followed by an extensive investigation into how those properties change when treated with potential inhibitors of spontaneous combustion.

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Appendix I

Description of Coal Samples

Table 1

Description of Coal Samples

Sample #	Location	Rank
coal-A	Alberta Foothills High volatile bituminous	hvb
coal-B	Alberta Foothills High volatile bituminous	hvb
coal-C	Alberta Foothills High volatile bituminous	hvb
coal-D	Alberta Plains Subbituminous	sub
coal-E	Alberta Plains Subbituminous	sub
coal-F	Alberta Plains Subbituminous	sub

Appendix II

Tables

Table 2

Petrographic Analyses of Coal Samples (on mmf basis)

Coal	Vitrinite %	Liptinite %[a]	Inertinite %
A	65.8	6.6	27.6
B	64.0	6.0	30.0
C	81.8	6.4	11.8
D	67.6	3.6	28.8
E	78.6	4.0	12.4
F	87.8	7.1	5.1

[a] Synonymous to Exinite.

Table 3

Proximate Analysis of Coal Samples

Coal	Equilibrium Moisture (%)	Volatile Matter (%) d[1]	Volatile Matter (%) daf[2]	Fixed Carbon (%) d	Fixed Carbon (%) daf	Ash (%)
A	7.50	36.35	39.22	56.33	60.78	7.32
B	7.48	37.10	40.00	55.66	60.00	7.24
C	11.91	36.46	41.00	52.47	59.00	11.07
D	18.40	36.53	39.30	56.41	60.70	7.06
E	20.20	32.80	41.09	47.03	58.91	20.17
F	24.60	39.17	41.96	54.18	58.04	6.65

[1] Dry.

[2] Dry ash free.

Table 4

Ultimate Analyses of Coal Samples

Coal	Carbon		Hydrogen		H/C	Nitrogen		Sulfur		Oxygen[3]		Ash
	d[1]	daf[2]	d[1]	daf		d	daf	d	daf	d	daf	
A	73.75	79.57	4.39	4.74	0.71	0.90	0.97	0.38	0.41	13.26	14.31	7.32
B	72.85	78.54	4.21	4.54	0.69	0.83	0.89	0.24	0.26	14.63	15.77	7.24
C	65.34	73.47	4.31	4.85	0.79	1.43	1.61	0.43	0.48	17.42	19.59	11.07
D	65.48	70.45	3.92	4.22	0.72	0.75	0.81	0.24	0.26	22.55	24.26	7.06
E	62.44	78.22	3.92	4.91	0.75	0.70	0.88	0.24	0.30	12.52	15.69	20.17
F	63.89	68.44	4.16	4.46	0.78	1.35	1.45	0.48	0.51	23.47	25.14	6.65

[1]dry
[2]dry ash free
[3]by difference

Table 5

Mineral Constituents in Coal Samples (ppm)

Mineral constituents	Coal A	B	C	D	E	F
Aluminum	11.68	94.9	32.8	88.6	72.9	64.9
Arsenic	< 25 ppb	< 25 ppb	< 25 ppb	< 25 ppb	< 25 ppb	< 25 ppb
Barium	0.34	0.19	0.55	0.28	0.38	0.29
Boron	0.15	0.10	0.30	0.17	0.24	0.34
Cadmium	0.007	0.03	0.01	0.02	0.02	0.02
Calcium	84.7	227.5	122.1	192.6	209.5	194.3
Chromium	< 4 ppb	0.04	0.02	0.01	0.02	0.03
Cobalt	< 2 ppb	0.10	0.03	0.05	0.09	0.08
Copper	< 2 ppb	0.02	< 2 ppb	0.05	0.08	< 2 ppb
Iron	4.09	48.37	9.00	48.27	46.27	42.27
Lead	0.08	0.32	0.13	0.25	0.24	0.29
Magnesium	2.85	16.8	4.65	8.56	14.6	6.61
Manganese	0.09	1.47	0.43	0.62	1.18	0.41
Molybdenum	< 5 ppb	0.01	< 5 ppb	< 5 ppb	< 5 ppb	< 5 ppb
Nickel	< 6 ppb	0.07	0.01	0.08	0.09	0.07
Phosphorous	0.15	0.68	0.37	0.81	0.57	3.47
Potassium	2.59	6.96	3.79	2.03	2.97	2.84
Selenium	< 20 ppb	< 20 ppb	< 20 ppb	< 20 ppb	< 20 ppb	< 20 ppb
Silicon	0.16	0.26	0.84	0.71	1.24	0.94
Silver	0.01	0.02	0.02	0.01	0.02	0.03
Sodium	3.51	2.07	< 10 ppb	31.1	0.95	63.19
Tin	< 6 ppb	0.90	0.28	< 6 ppb	< 6 ppb	< 6 ppb
Titanium	0.59	4.37	1.40	1.83	1.29	2.25
Vanadium	0.02	0.1	0.04	0.04	0.04	0.03
Zinc	< 2 ppb	0.04	< 2 ppb	0.01	0.04	0.02

Table 6

Temperature rise (°C) with varying equilibrium moisture deficiencies with High Volatile Bituminous Coal A when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 7.5%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
7.5	21.0	19.7	19.6	19.6	19.7	19.7	19.8	-1.2
6.06	21.0	20.8	20.8	20.7	20.6	20.5	20.2	-0.8
5.32	21.0	21.3	21.5	21.6	21.6	21.6	21.6	+0.6
4.24	21.0	22.2	23.5	24.5	25.1	25.6	25.9	+4.9
3.36	21.0	22.8	24.3	25.5	26.5	27.3	27.9	+6.9

[1] Moist air flow at the rate of 150 ml/min.

Table 7

Temperature rise (°C) with varying equilibrium moisture deficiencies with High Volatile Bituminous Coal B when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 7.48%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
7.48	21.0	20.4	20.4	20.5	20.7	20.7	20.8	-0.2
5.95	21.0	21.4	21.7	22.0	21.9	21.7	21.6	+0.6
5.08	21.0	22.1	22.9	23.4	23.8	24.0	24.1	+3.1
3.98	21.0	22.6	24.2	25.5	26.5	27.2	27.6	+6.6
2.83	21.0	22.9	24.9	26.9	28.4	29.7	30.7	+9.7

[1] Moist air flow at the rate of 150 ml/min.

Table 8

Temperature rise (°C) with varying equilibrium moisture deficiencies with High Volatile Bituminous Coal C when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 11.91%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
11.91	21.0	19.8	20.1	20.3	20.4	20.8	20.9	-0.1
10.91	21.0	21.9	21.9	22.1	22.1	22.1	22.1	+1.1
9.17	21.0	21.7	22.0	22.1	22.1	22.0	21.8	+0.8
8.19	21.0	21.6	22.0	22.4	22.6	22.7	22.8	+1.8
6.66	21.0	22.3	23.3	24.2	24.9	25.5	25.8	+4.8
3.53	21.0	23.1	25.1	26.9	28.7	30.3	31.6	+10.6

[1] Moist air flow at the rate of 150 ml/min.

Table 9

Temperature rise (°C) with varying equilibrium moisture deficiencies with Subbituminous Coal D when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 18.4%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
18.4	21.0	19.8	19.8	19.9	20.0	20.2	20.2	-0.8
15.7	21.0	20.7	20.9	20.7	20.8	20.7	20.8	-0.2
14.14	21.0	21.0	21.1	21.2	21.3	21.4	21.5	+0.5
11.06	21.0	21.8	22.5	22.9	23.2	23.4	23.6	+2.6
9.36	21.0	22.0	22.8	23.7	24.3	24.8	25.2	+4.2
7.06	21.0	22.5	24.2	25.7	27.5	28.4	29.3	+8.3

[1] Moist air flow at the rate of 150 ml/min.

Table 10

Temperature rise (°C) with varying equilibrium moisture deficiencies with Subbituminous Coal E when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 20.2%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
20.2	21.0	20.0	20.0	20.2	20.4	20.6	20.8	-0.2
17.18	21.0	21.0	20.9	21.0	21.0	20.9	21.0	0.0
15.26	21.0	21.9	21.9	21.9	22.1	22.3	22.2	+1.2
12.00	21.0	21.8	22.5	23.1	23.5	23.7	24.0	+3.0
10.10	21.0	24.1	26.0	27.2	28.1	28.5	28.7	+7.7
7.65	21.0	25.2	27.7	29.7	31.6	32.6	33.5	+12.5

[1] Moist air flow at the rate of 150 ml/min.

Table 11

Temperature rise (°C) with varying equilibrium moisture deficiencies with Subbituminous Coal F when treated with moist (~ 60% RH) air.[1]

[Coal equilibrium moisture: 24.6%]

Moisture %	Time (min.) 0	30	60	90	120	150	180	Total change (°C)
	Temperature (°C)							
24.6	21.0	19.9	19.7	19.7	19.6	19.6	19.5	-1.5
21.71	21.0	20.5	20.2	20.2	20.2	20.2	20.3	-0.7
18.04	21.0	20.9	20.8	20.8	20.8	20.8	20.7	-0.3
14.60	21.0	21.2	21.3	21.4	21.5	21.6	21.7	+0.7
12.10	21.0	21.3	21.5	21.7	21.8	21.9	22.0	+1.0
9.74	21.0	21.9	22.7	23.2	23.8	24.1	24.4	+3.4
7.55	21.0	22.1	23.2	24.3	25.2	26.0	26.5	+5.5
2.72	21.0	23.1	25.4	27.9	30.2	32.4	34.4	+13.4

[1] Moist air flow at the rate of 150 ml/min.

Table 12

Peroxygen Analyses of High Volatile Bituminous Coal A

[Coal equilibrium moisture: 7.5%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air (~ 60% RH)
7.5	0.18×10^{-5}	0.15×10^{-5}
6.1	0.26×10^{-5}	0.26×10^{-5}
5.3	0.30×10^{-5}	0.29×10^{-5}
4.24	0.23×10^{-5}	0.27×10^{-5}
3.36	0.32×10^{-5}	0.39×10^{-5}

Moist air flow at the rate of 150 ml/min.

Table 13

Peroxygen Analyses of High Volatile Bituminous Coal B

[Coal equilibrium moisture: 7.48%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air (~ 60% RH)
7.48	0.26×10^{-5}	0.31×10^{-5}
5.95	0.34×10^{-5}	0.32×10^{-5}
5.08	0.47×10^{-5}	0.52×10^{-5}
3.98	0.41×10^{-5}	0.49×10^{-5}
2.83	0.32×10^{-5}	0.26×10^{-5}

Moist air flow at the rate of 150 ml/min.

Table 14

Peroxygen Analyses of High Volatile Bituminous Coal C

[Coal equilibrium moisture: 11.91%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air[1] (~ 60% RH)
11.91	0.28×10^{-5}	0.24×10^{-5}
10.91	0.23×10^{-5}	0.20×10^{-5}
9.17	0.26×10^{-5}	0.22×10^{-5}
8.19	0.24×10^{-5}	0.20×10^{-5}
6.66	0.29×10^{-5}	0.30×10^{-5}
3.53	0.38×10^{-5}	0.34×10^{-5}

[1] Moist (~ 60% RH) air at the flow rate of 150 ml/min.

Table 15

Peroxygen Analyses of Subbituminous Coal D

[Coal equilibrium moisture: 18.4%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air (~ 60% RH)
18.4	0.54×10^{-5}	0.59×10^{-5}
15.7	0.72×10^{-5}	0.73×10^{-5}
14.14	0.78×10^{-5}	0.72×10^{-5}
11.06	0.95×10^{-5}	0.75×10^{-5}
9.36	0.83×10^{-5}	0.82×10^{-5}
7.06	1.03×10^{-5}	0.84×10^{-5}

Moist air flow at the rate of 150 ml/min.

Table 16

Peroxygen Analyses of Subbituminous Coal E

[Coal equilibrium moisture: 20.2%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air (~ 60% RH)
20.2	0.43×10^{-5}	0.46×10^{-5}
17.18	0.52×10^{-5}	0.52×10^{-5}
15.26	0.57×10^{-5}	0.58×10^{-5}
12.00	0.38×10^{-5}	0.35×10^{-5}
10.1	0.40×10^{-5}	0.49×10^{-5}
7.65	0.64×10^{-5}	0.62×10^{-5}

Moist air flow at the rate of 150 ml/min.

Table 17

Peroxygen Analyses of Subbituminous Coal F

[Coal equilibrium moisture: 24.6%]

Moisture %	Peroxygen g/g coal	
	Before treating with moist air (~ 60% RH)	After treating with moist air (~ 60% RH)
24.6	1.16×10^{-5}	1.18×10^{-5}
21.71	0.83×10^{-5}	1.01×10^{-5}
18.04	0.87×10^{-5}	0.89×10^{-5}
14.60	0.62×10^{-5}	0.73×10^{-5}
12.1	0.68×10^{-5}	0.72×10^{-5}
9.74	0.88×10^{-5}	0.65×10^{-5}
7.55	0.67×10^{-5}	1.03×10^{-5}
2.72	1.11×10^{-5}	1.13×10^{-5}

Moist air flow at the rate of 150 ml/min.

Table 18

Porosity Study of High Volatile Bituminous Coal C

[Coal equilibrium moisture: 11.91%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters		
		Radius A°	Volume cc/g	Area m^2/g
11.91	a	>30	0.0641	11.86
		<30	0.0127	10.76
	b	>30	0.0551	11.17
		<30	0.0135	11.49
6.66	a	>30	0.0603	11.89
		<30	0.0135	11.48
	b	>30	0.0605	10.79
		<30	0.0125	10.51
3.53	a	>30	0.0611	11.64
		<30	0.0157	13.38
	b	>30	0.0668	12.87
		<30	0.0161	13.88

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

Table 19

Porosity Study of Subbituminous Coal D

[Coal equilibrium moisture: 18.4%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters		
		Radius A°	Volume cc/g	Area m^2/g
18.4	a	>30	0.0637	11.36
		<30	0.0131	11.06
	b	>30	0.0742	10.54
		<30	0.0108	9.26
11.06	a	>30	0.0820	12.50
		<30	0.0113	9.69
	b	>30	0.0856	13.48
		<30	0.0154	13.13
7.06	a	>30	0.0851	13.13
		<30	0.0154	12.95
	b	>30	0.0879	14.56
		<30	0.0149	12.56

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

Table 20

Porosity Study of Subbituminous Coal F

[Coal equilibrium moisture: 24.6%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters		
		Radius A°	Volume cc/g	Area m^2/g
24.6	a	>30	0.0645	9.590
		<30	0.0114	9.76
	b	>30	0.0730	11.53
		<30	0.012	10.38
7.55	a	>30	0.0860	16.90
		<30	0.0174	14.61
	b	>30	0.0867	17.73
		<30	0.0185	15.56
2.72	a	>30	0.0876	17.46
		<30	0.0248	21.05
	b	>30	0.0867	16.27
		<30	0.0230	19.84

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

Table 21

E.P.R. Study of High Volatile Bituminous Coal C

[Coal equilibrium moisture: 11.91%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters			
		g-factor	Area	ΔHpp	$\Delta H_{1/2}$
11.91	a	2.00216	0.0120802	7.05463	10.7182
	b	2.00216	0.0120912	6.97002	10.3089
6.66	a	2.00218	0.0142644	7.14459	10.5311
	b	2.00223	0.0131274	7.14833	10.5379
3.53	a	2.00240	0.0165374	7.41493	10.7688
	b	2.00235	0.0157324	7.37257	10.5843

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

ΔHpp = Line-width - peak to peak.

$\Delta H_{1/2}$ = Half-line width.

Table 22

E.P.R. Study of Subbituminous Coal D

[Coal equilibrium moisture: 18.4%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters			
		g-factor	Area	ΔHpp	$\Delta H_{1/2}$
18.4	a	2.00235	0.00755942	6.79901	9.6356
	b	2.00260	0.00792354	6.58584	9.61129
11.06	a	2.00217	0.0124225	6.45425	10.1037
	b	2.00234	0.0121632	6.71924	10.0284
7.06	a	2.00240	0.0134561	7.06278	10.419
	b	2.00212	0.0123656	6.79758	10.4075

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

ΔHpp = Line-width - peak to peak.

$\Delta H_{1/2}$ = Half-line width.

Table 23

E.P.R. Study of Subbituminous Coal F

[Coal equilibrium moisture: 24.6%]

Moisture %	Moist air (~ 60% RH) treatment	Parameters			
		g-factor	Area	ΔHpp	$\Delta H_{1/2}$
24.6	a	2.00238	0.00526546	6.88764	9.58976
	b	2.00237	0.00554298	6.72634	9.65751
7.55	a	2.00267	0.00908417	7.40537	10.5137
	b	2.00248	0.00646495	7.31943	10.1432
2.72	a	2.00272	0.0114104	7.41093	11.0056
	b	2.00259	0.00884939	7.24658	10.6703

a = Before the treatment with moist air flow at the rate of 150 ml/min.

b = After the treatment with moist air flow at the rate of 150 ml/min.

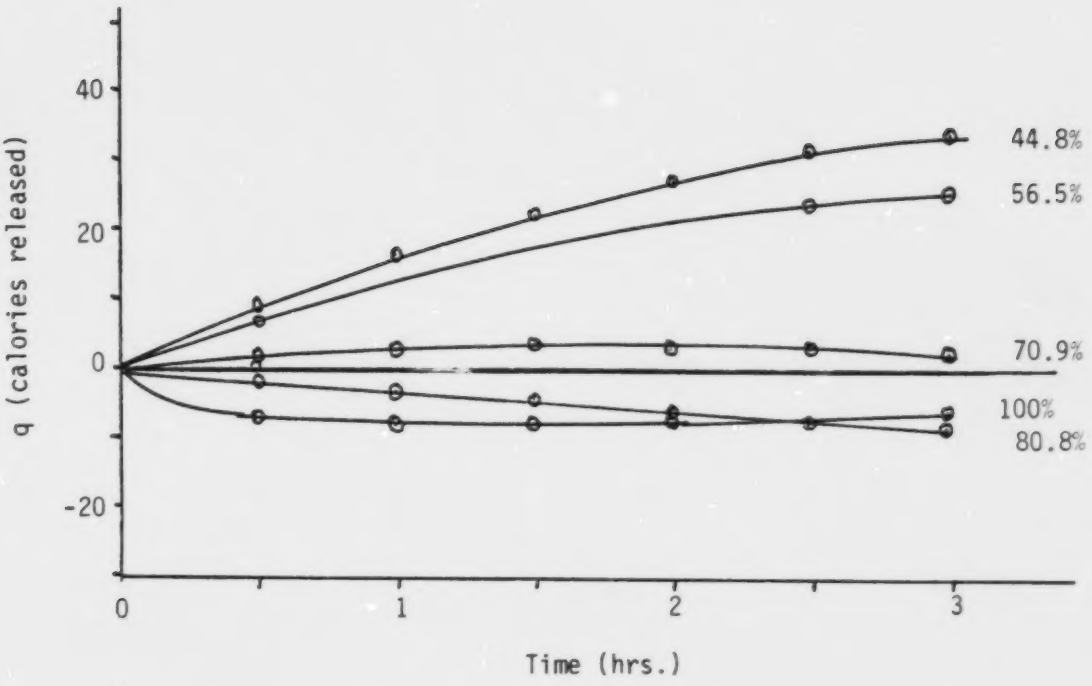
ΔHpp = Line-width - peak to peak.

$\Delta H_{1/2}$ = Half-line width.

Appendix III

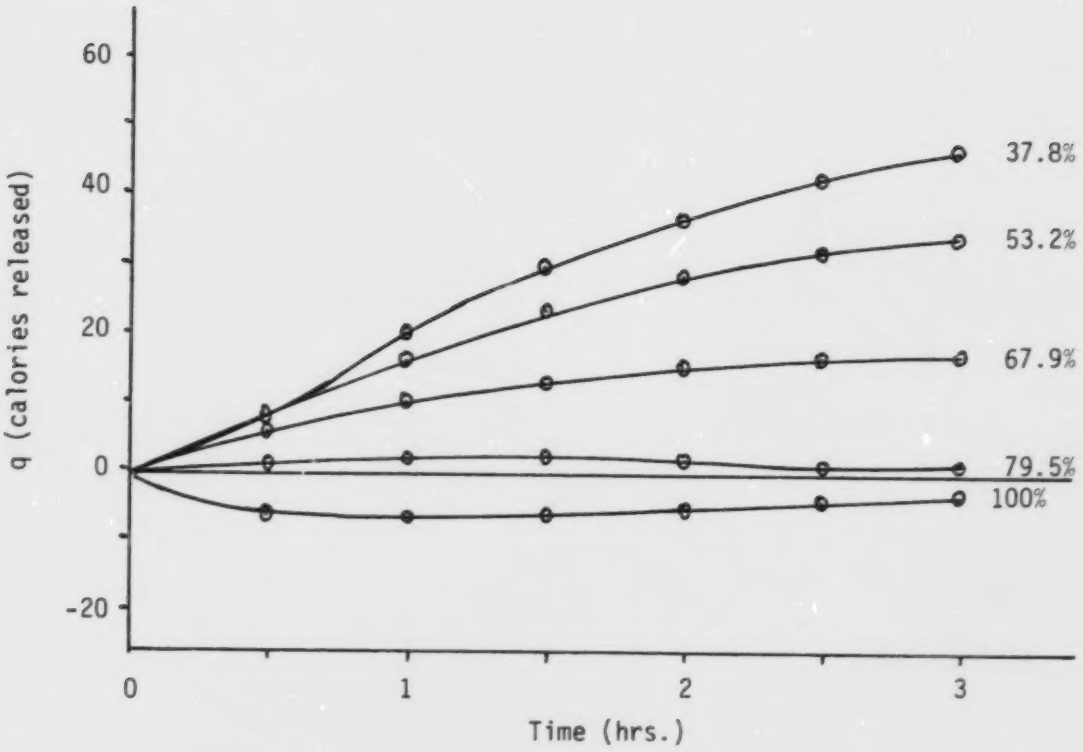
Figures

Figure 1



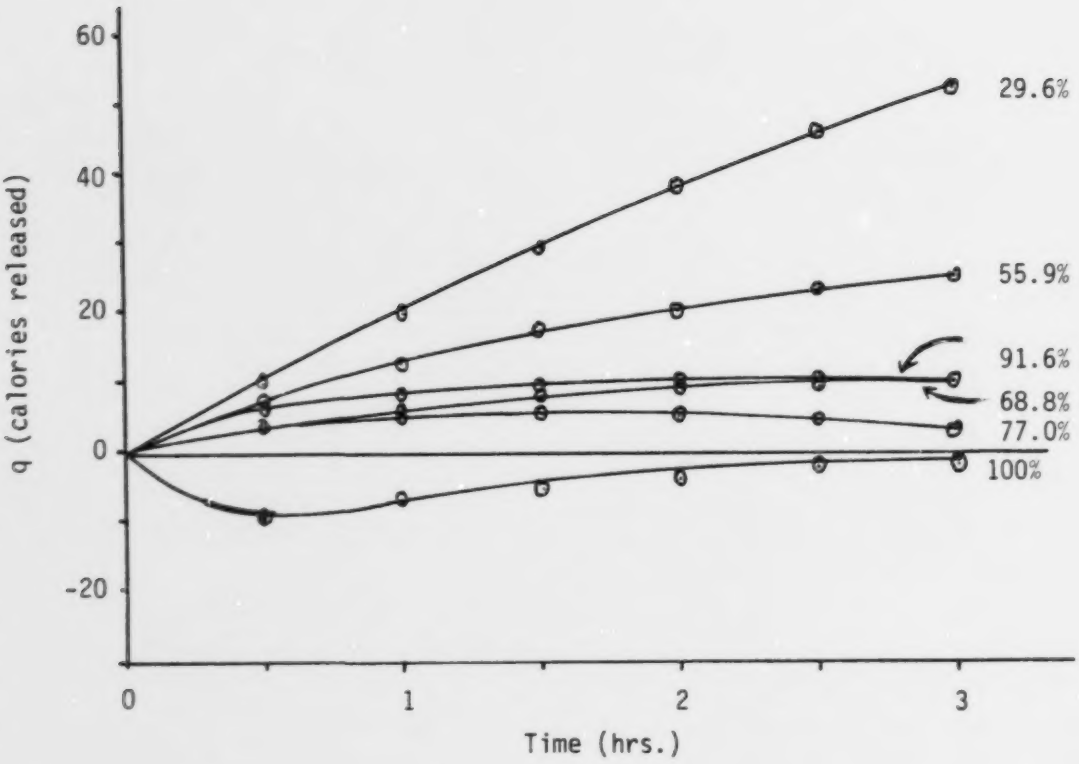
Thermal response of Coal A to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 2



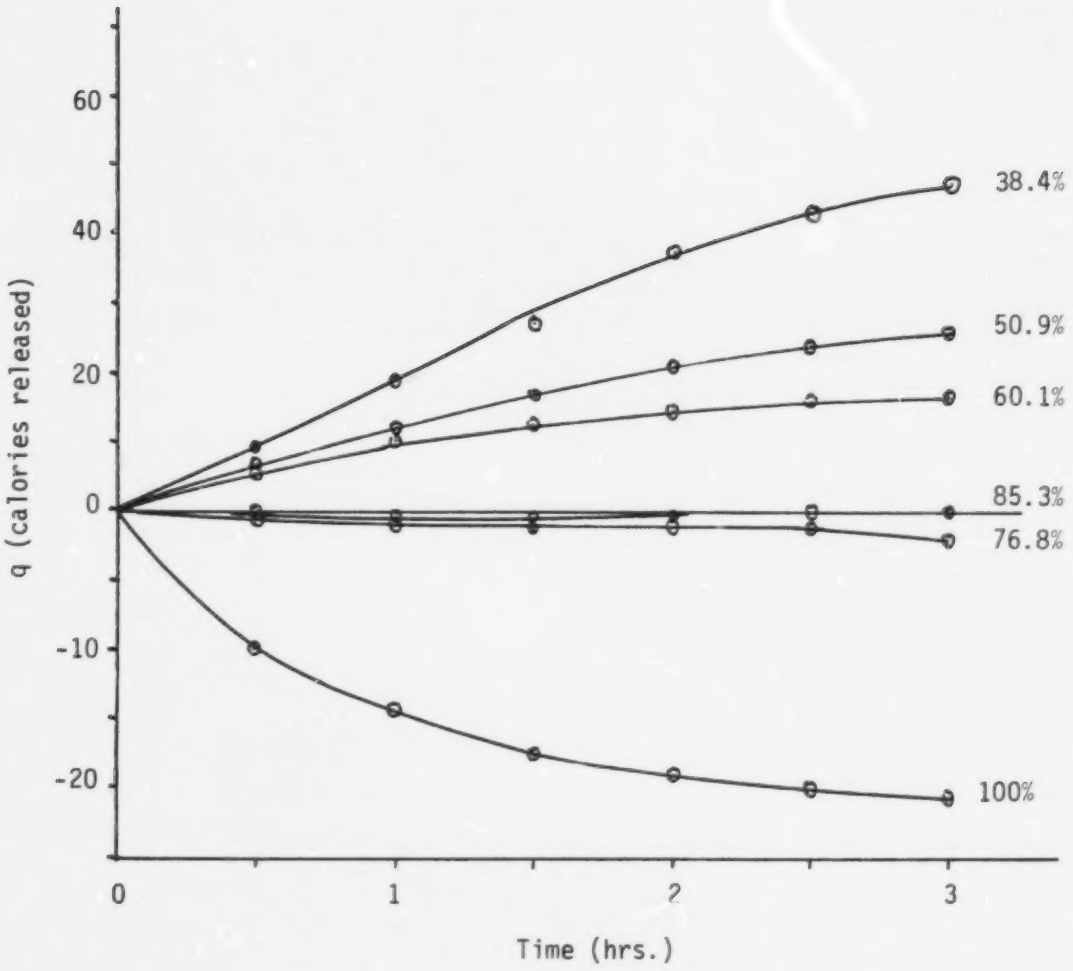
Thermal response of Coal B to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 3



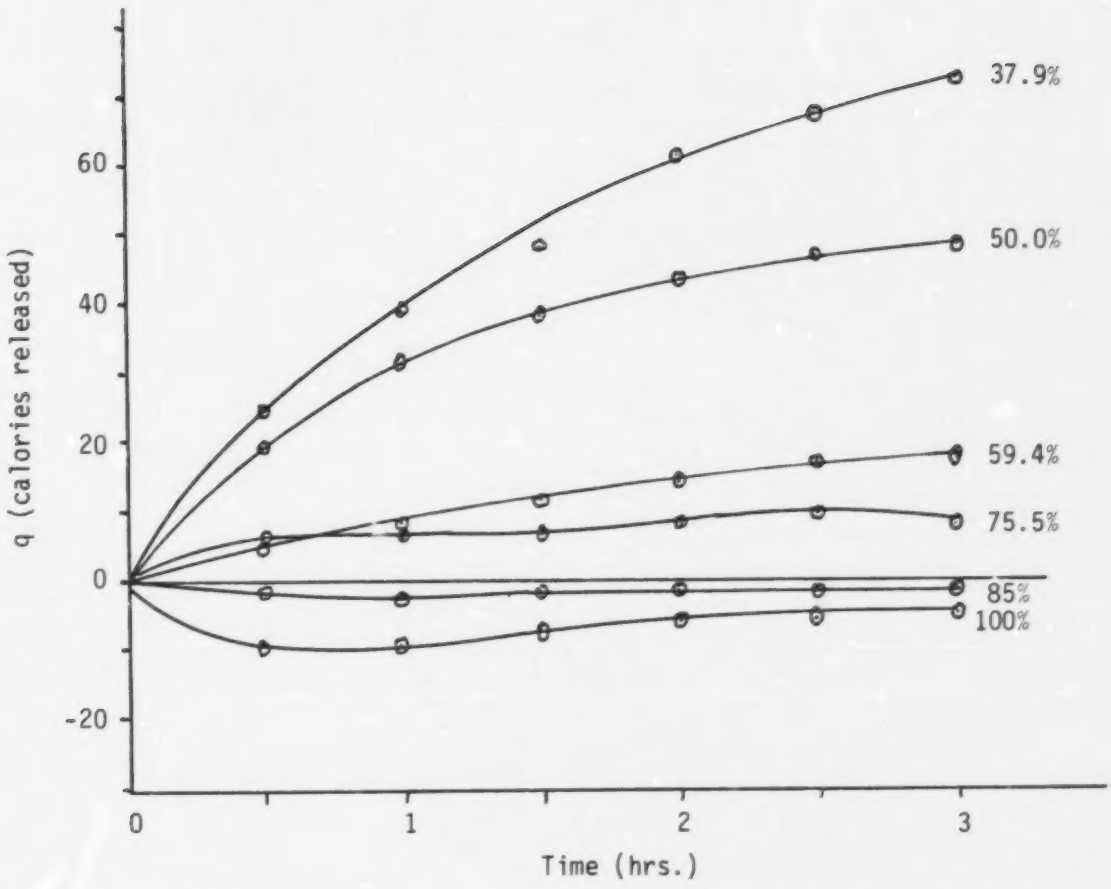
Thermal response of Coal C to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 4



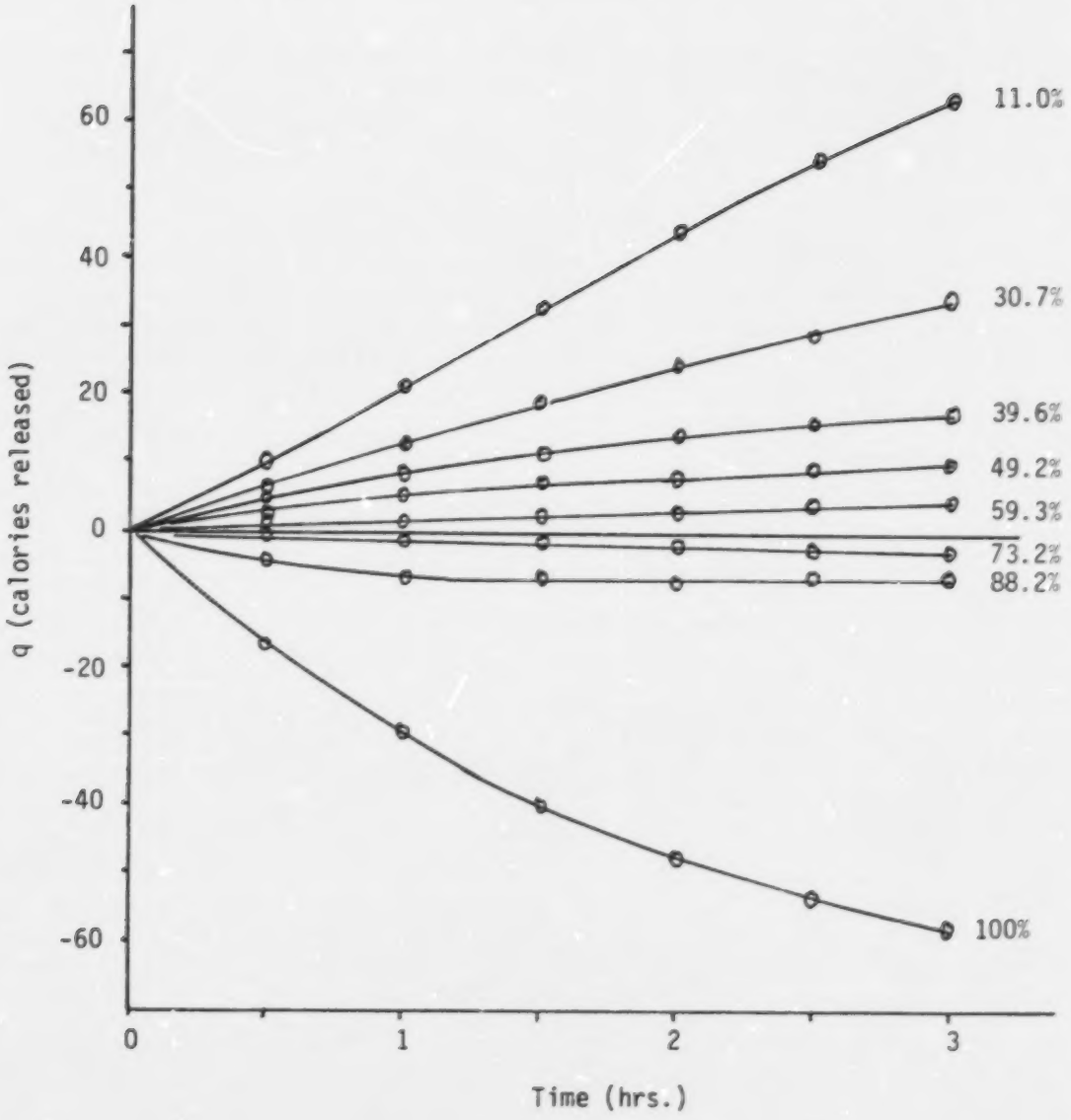
Thermal response of Coal D to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 5



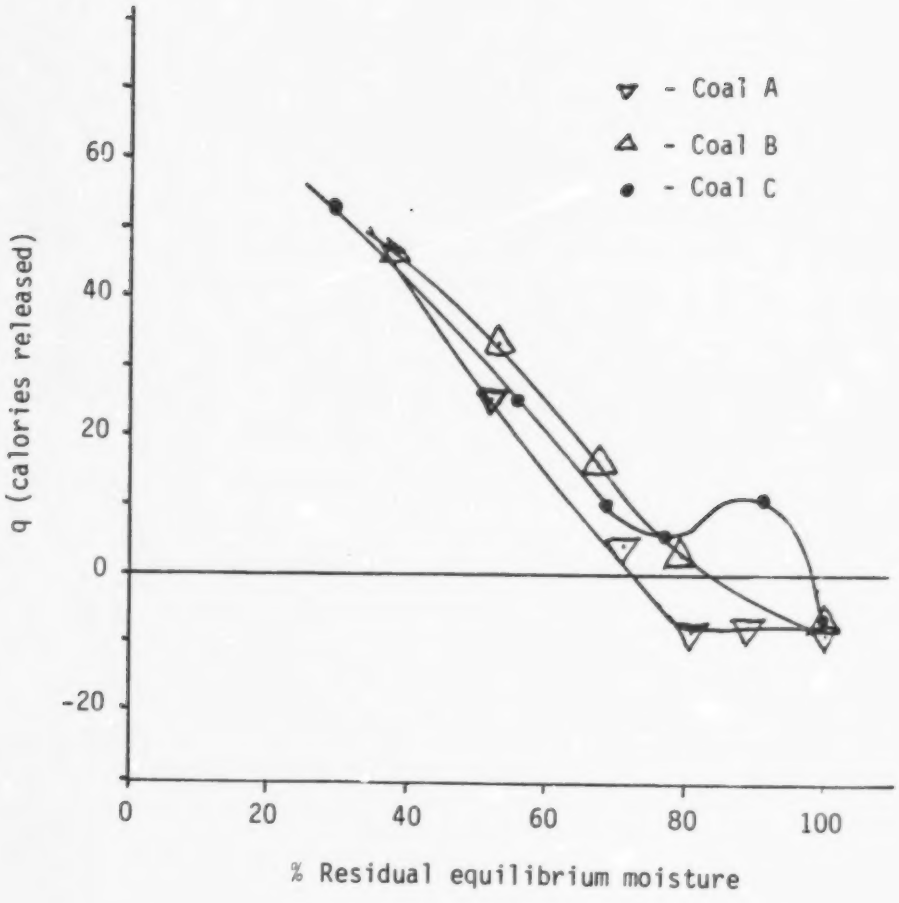
Thermal response of Coal E to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 6



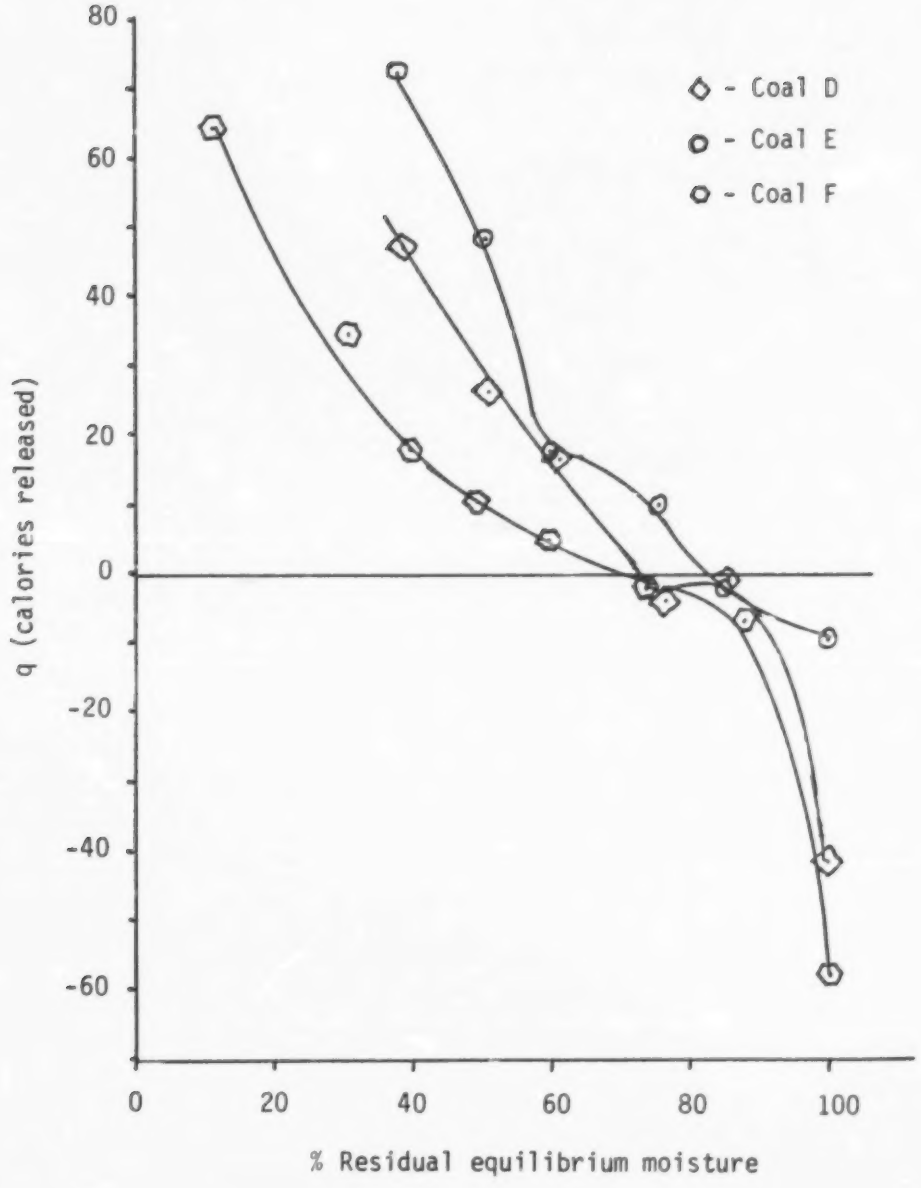
Thermal response of Coal F to 60% R.H. air flow.
(Percentages refer to residual equilibrium moisture.)

Figure 7

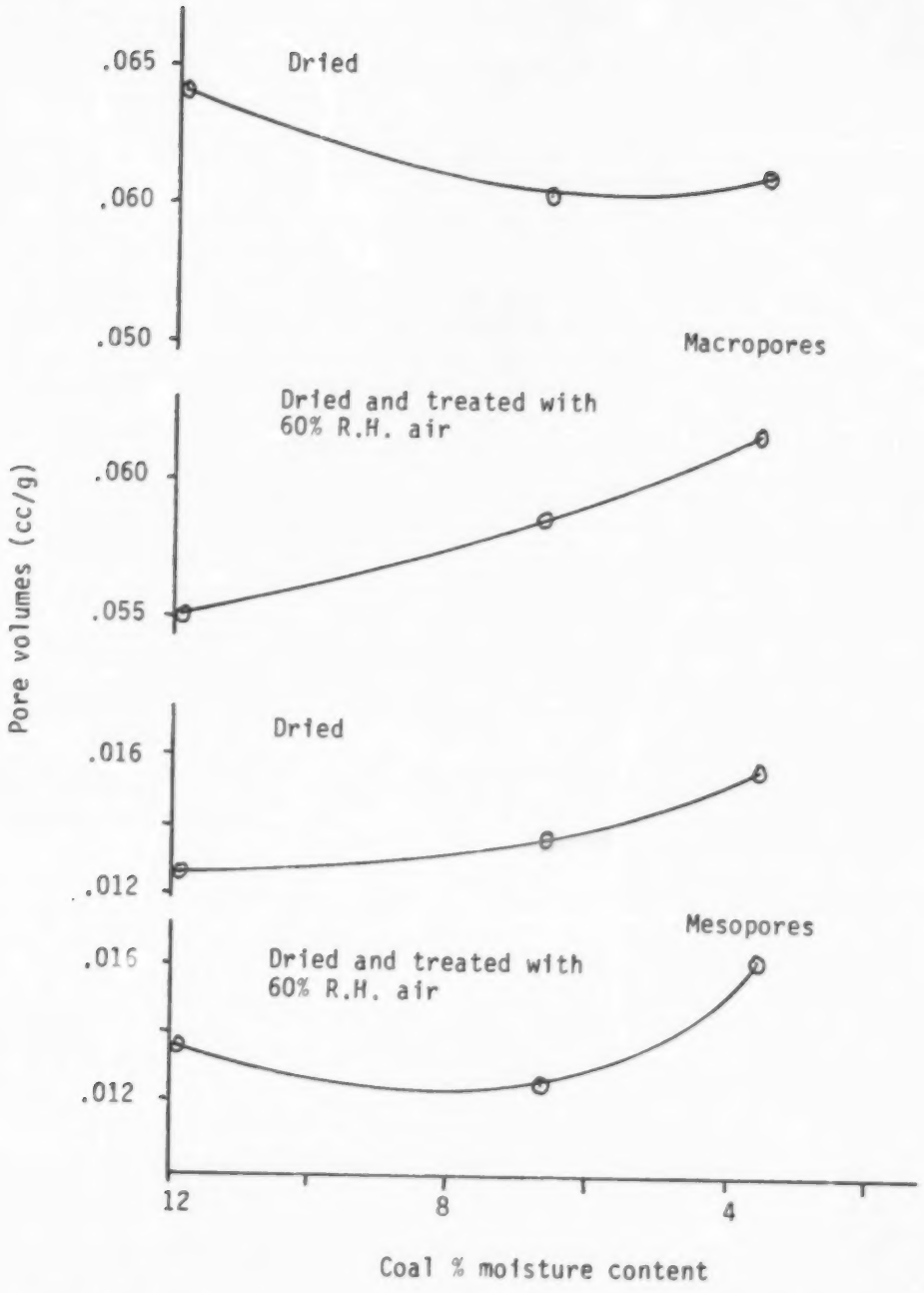


Thermal response of high volatile bituminous coals to 60% R.H. air flow after 3 hours.

Figure 8

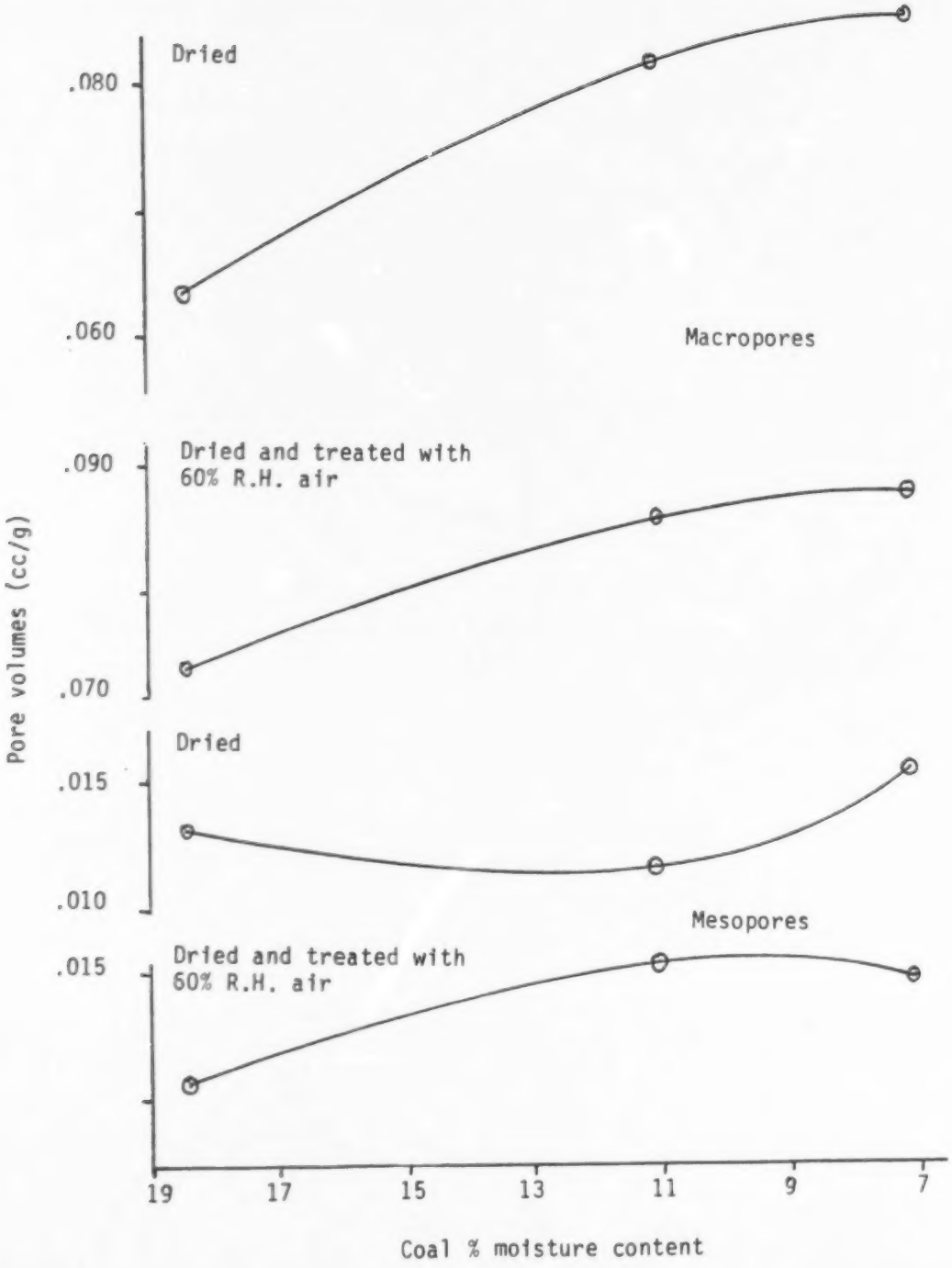


Thermal response of subbituminous coals to 60% R.H. air flow after 3 hours.



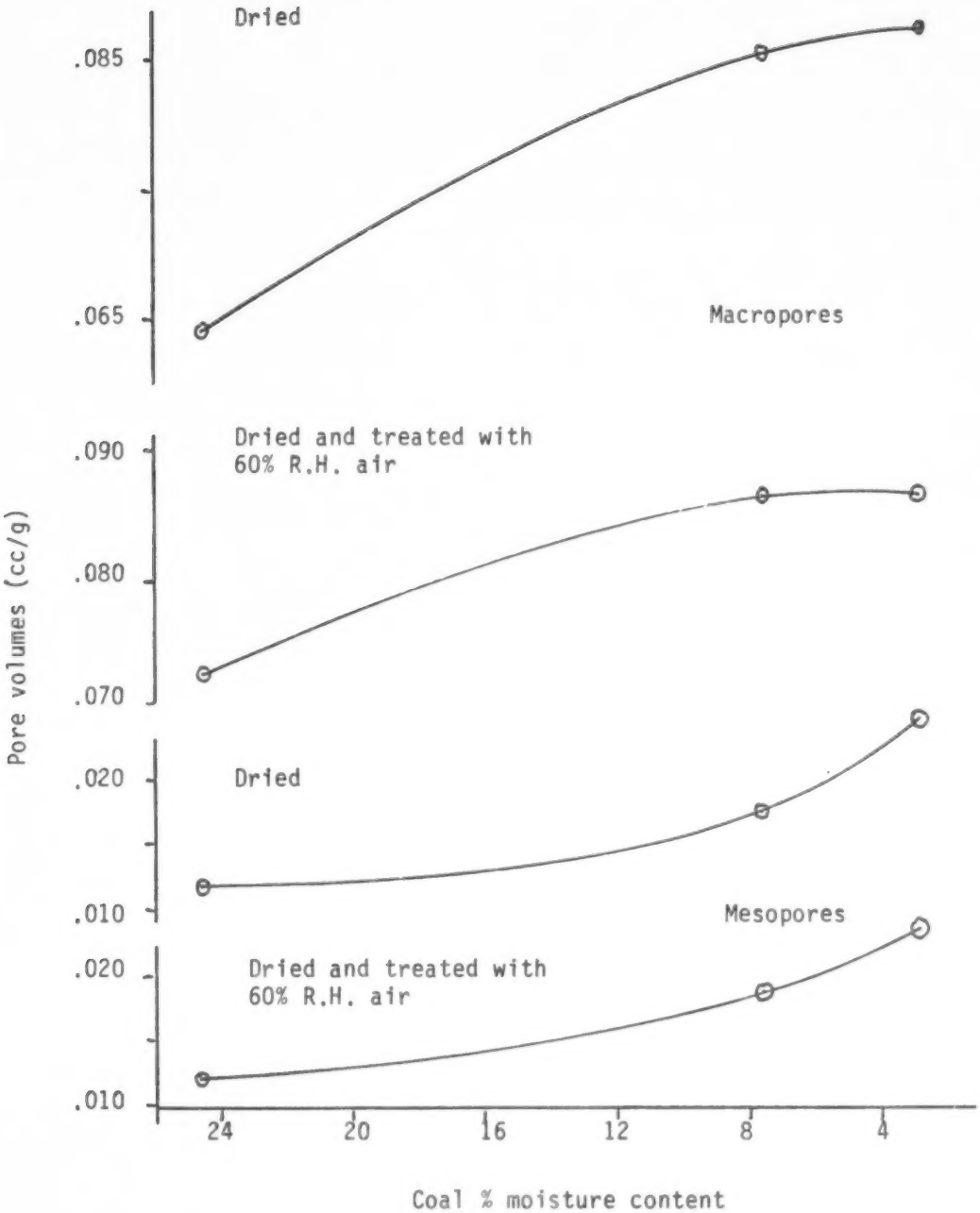
Changes in pore volumes with drying of Coal sample C.

Figure 9



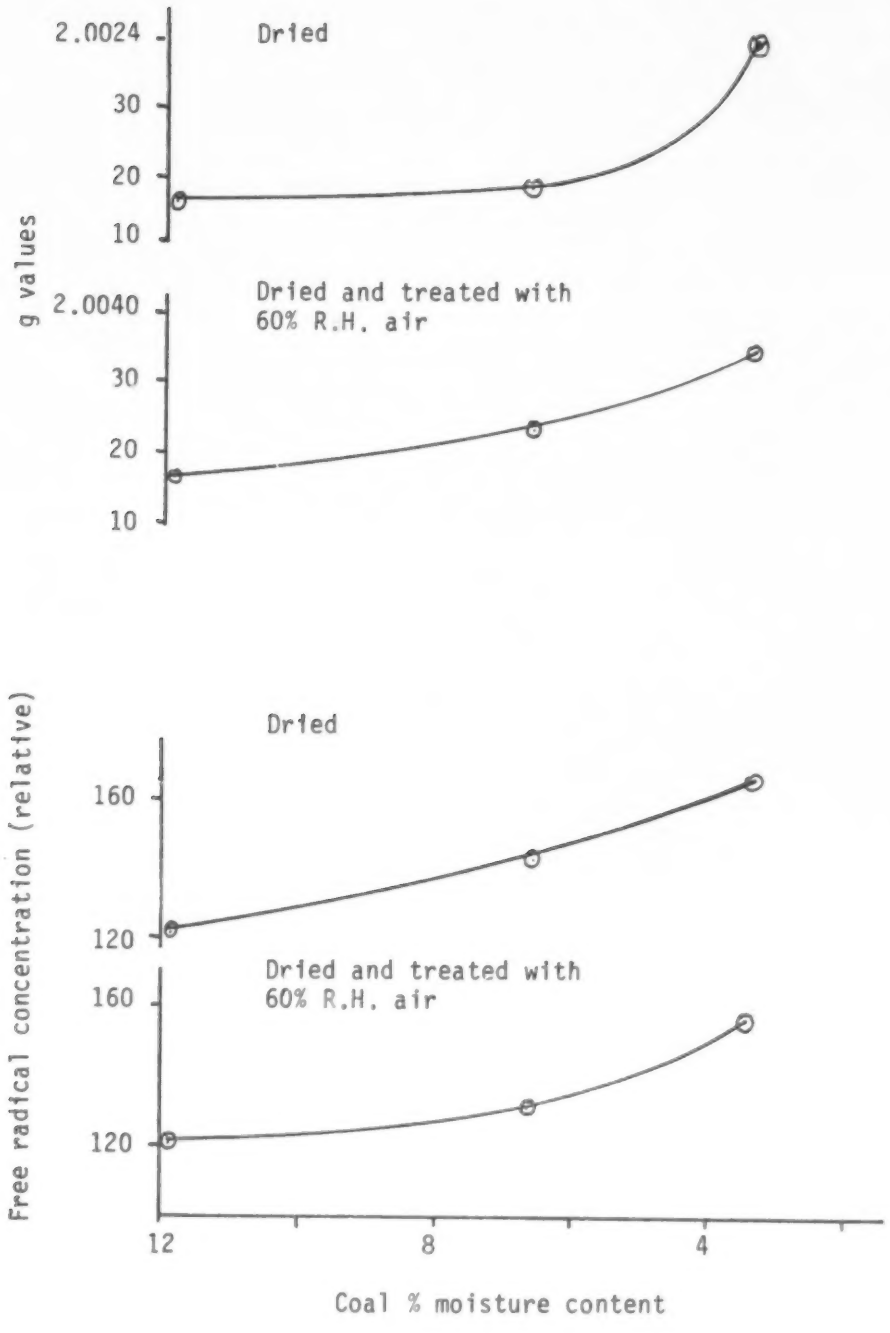
Changes in pore volumes with drying of Coal sample D.

Figure 10



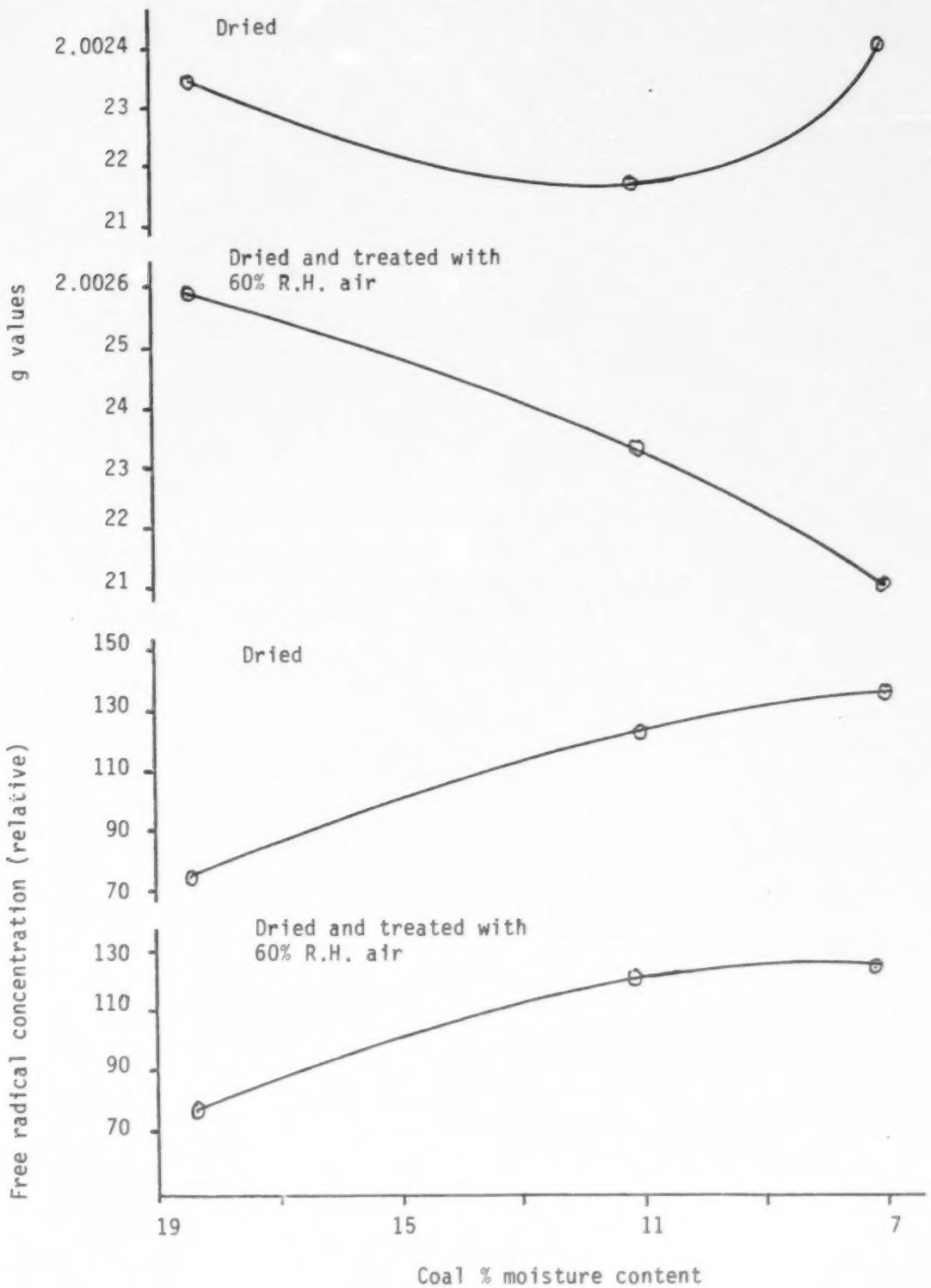
Changes in pore volumes with drying of Coal sample F.

Figure 11



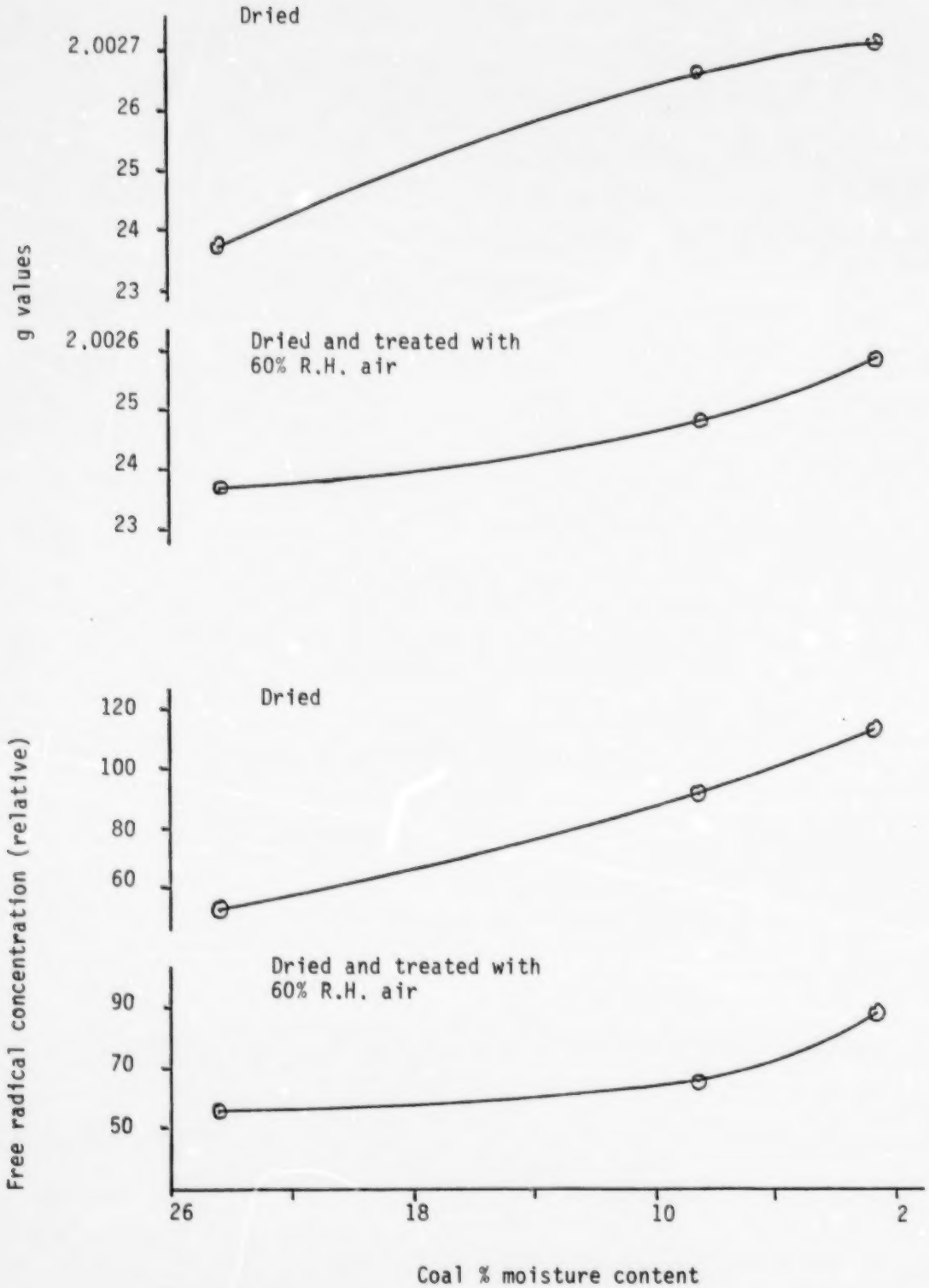
Changes in g values and relative free radical concentration of Coal C with drying.

Figure 12



Changes in g values and relative free radical concentration of Coal D with drying.

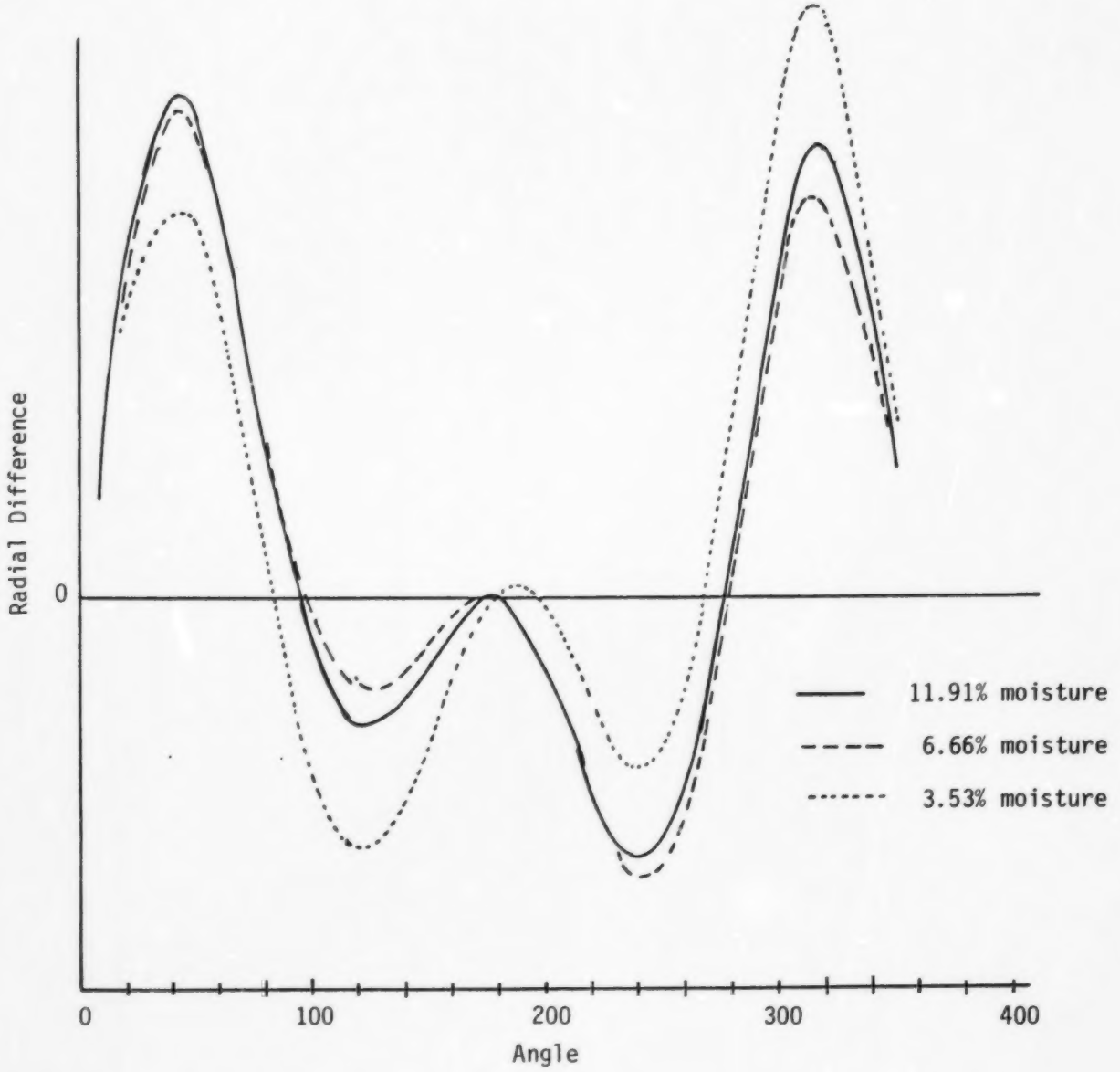
Figure 13



Changes in g value and relative free radical concentration of coal F with drying.

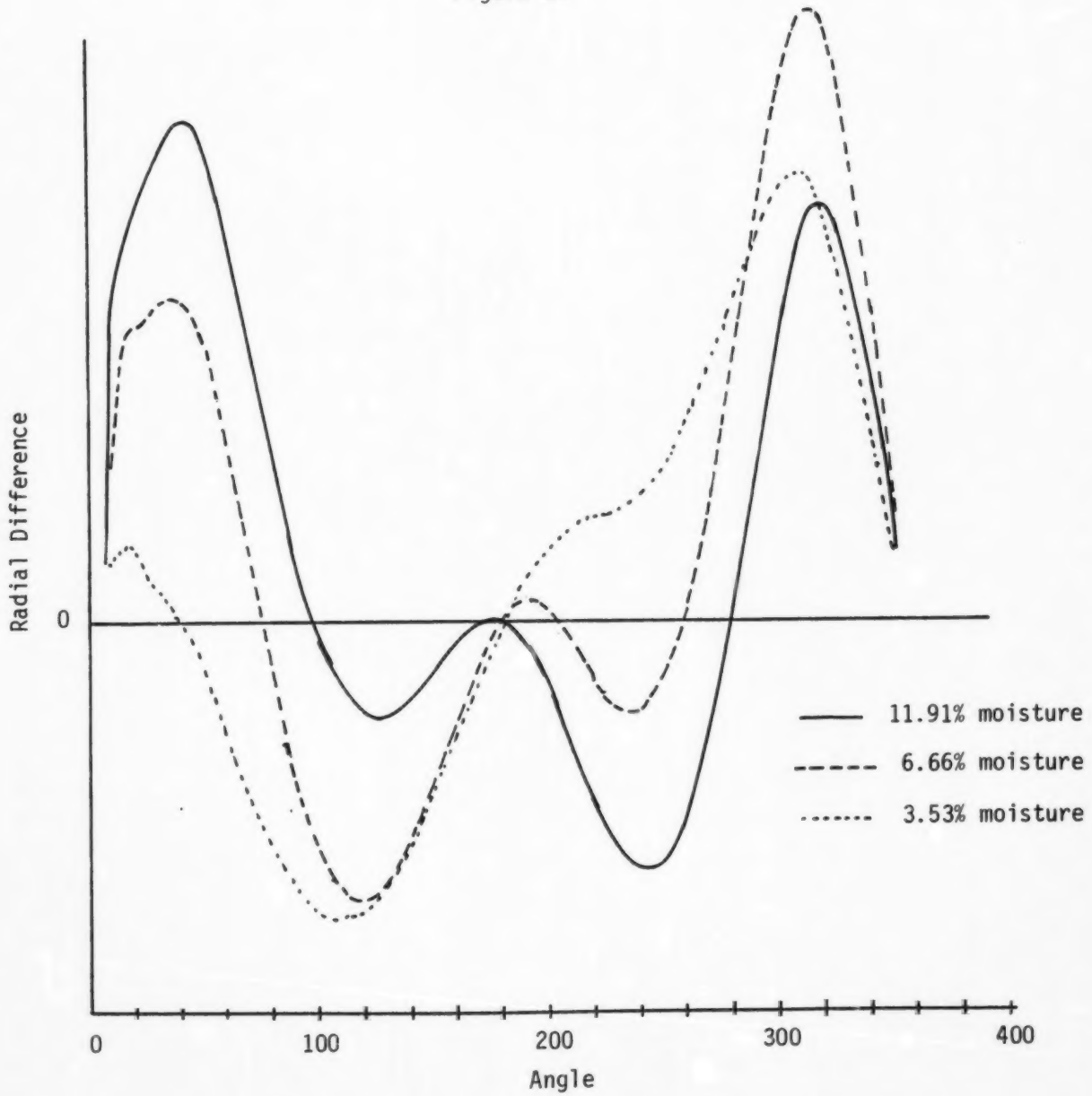
Figure 14

Figure 15



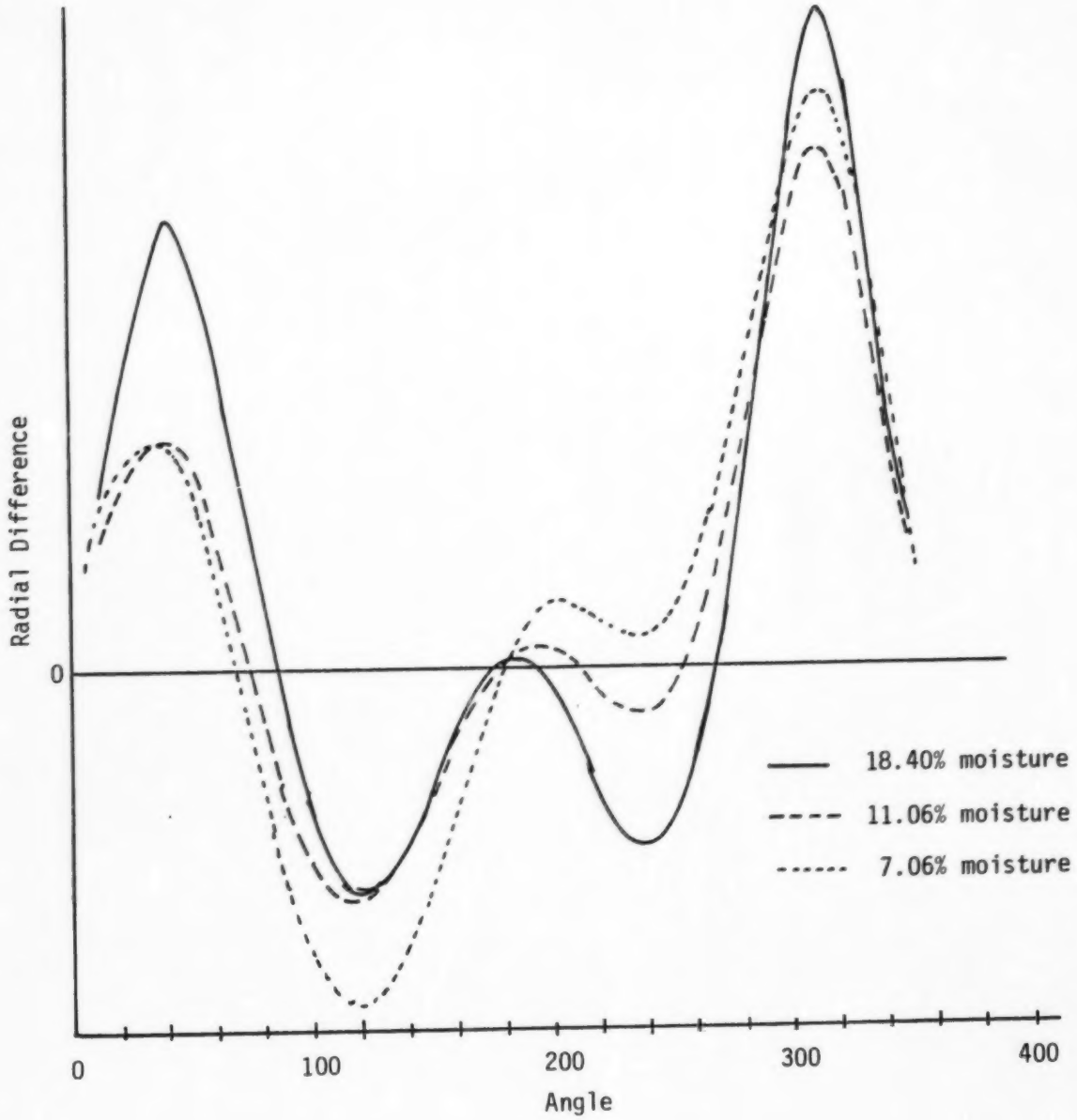
Argand dispersion diagram of dried Coal C samples.

Figure 16



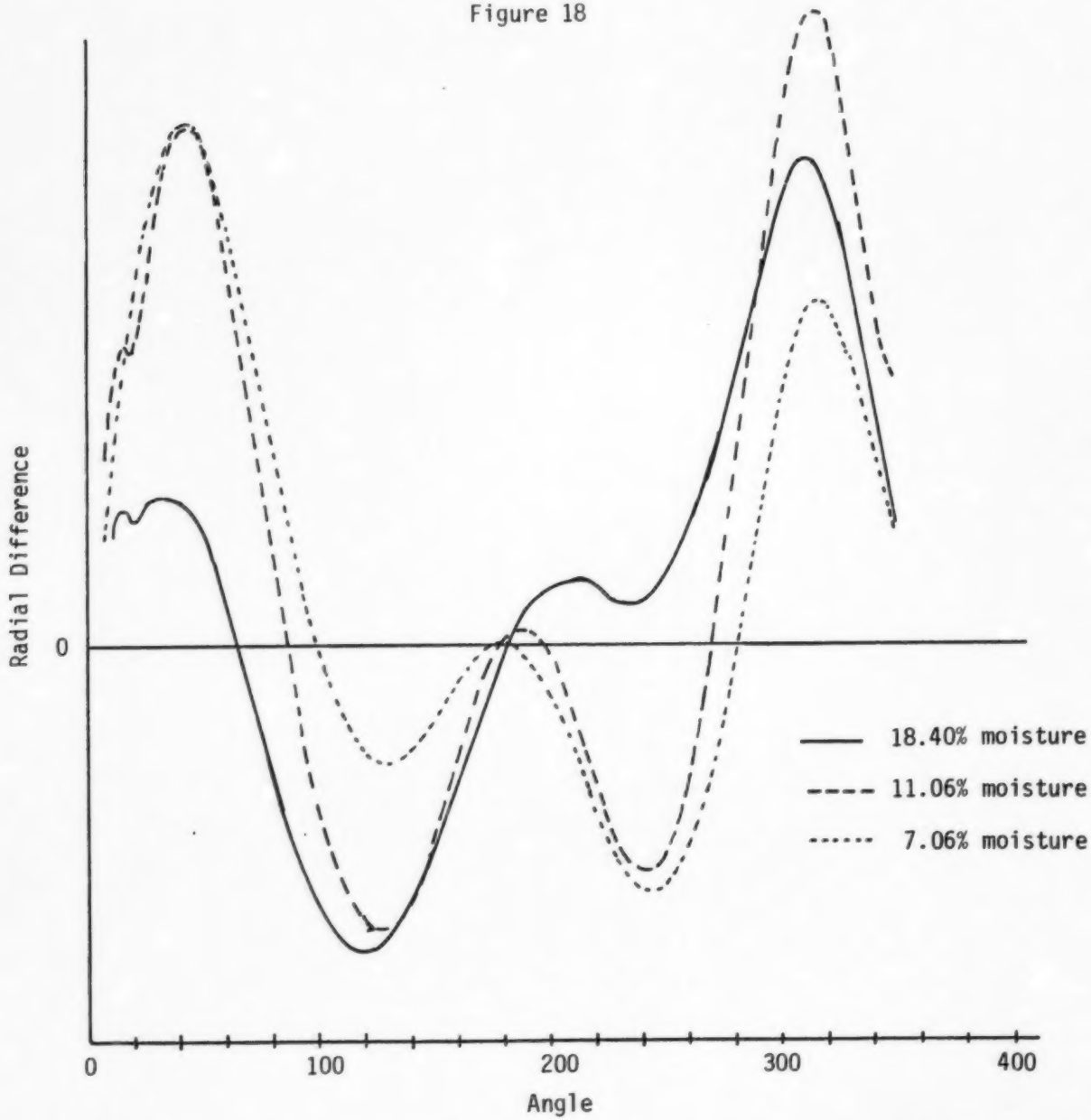
Argand dispersion diagram of dried Coal C samples treated with 60% R.H. air.

Figure 17



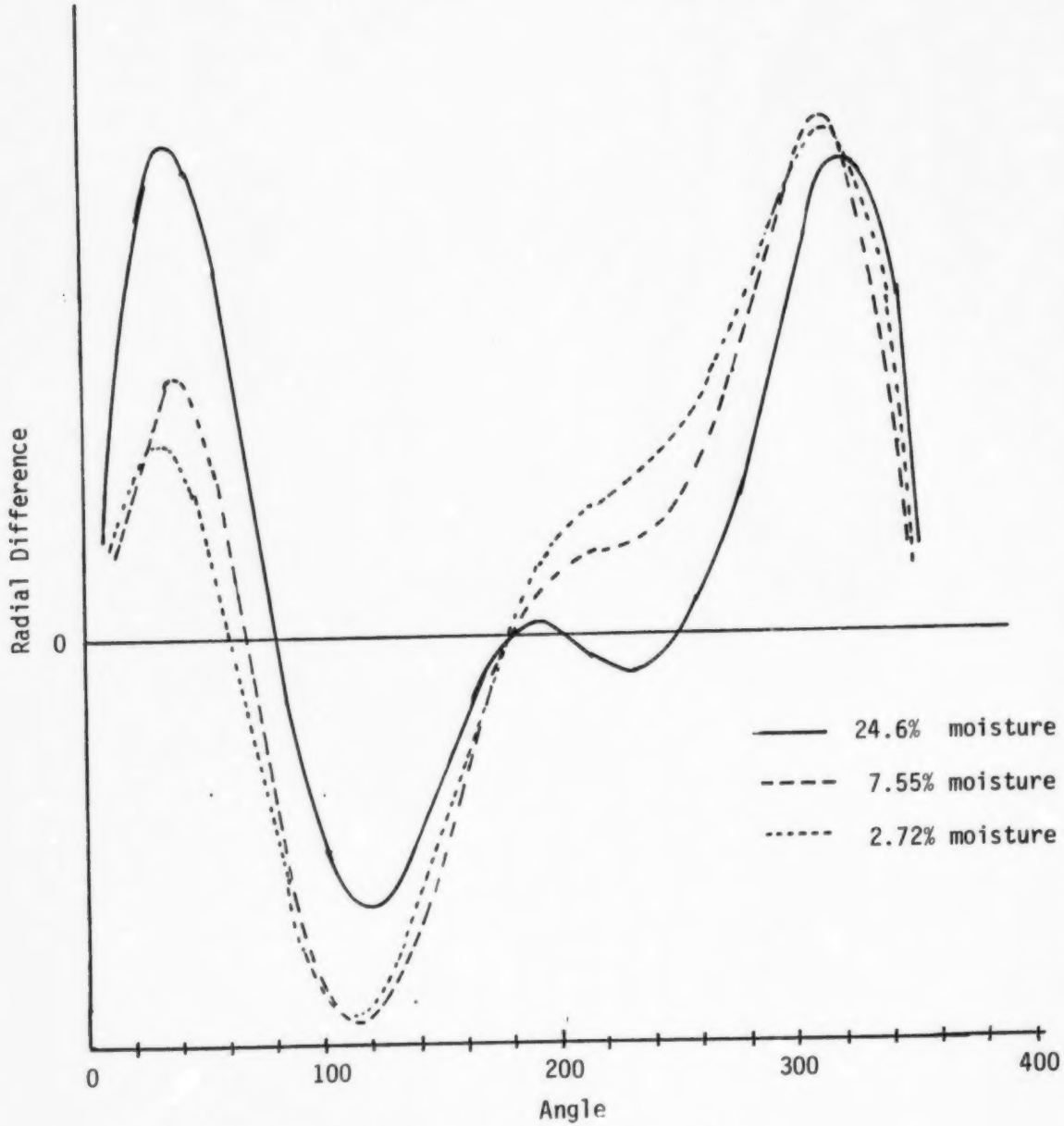
Argand dispersion diagram of dried Coal D samples.

Figure 18



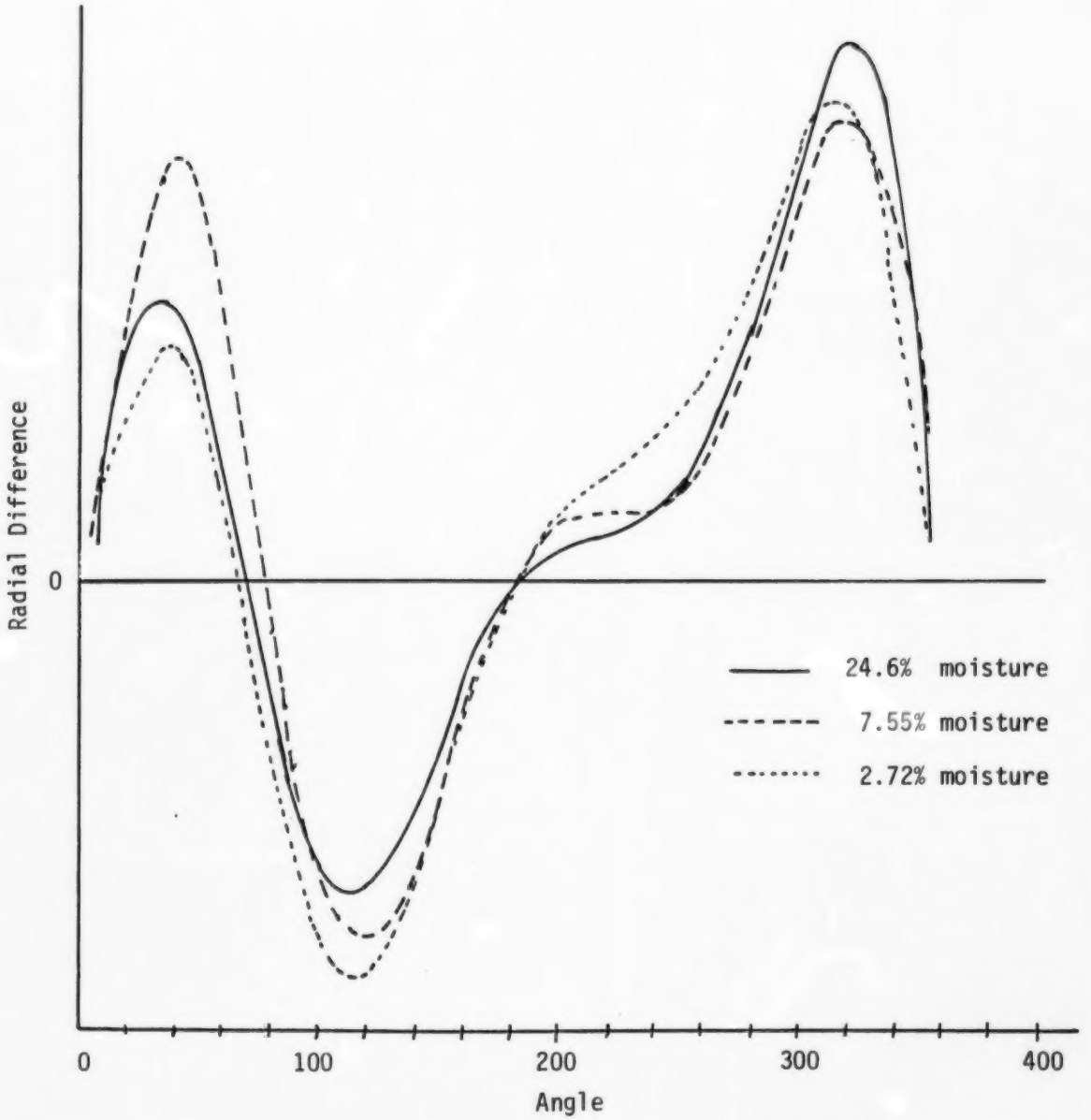
Argand dispersion diagram of dried Coal D samples treated with 60% R.H. air.

Figure 19



Argand dispersion diagram of dried Coal F samples.

Figure 20



Argand dispersion diagram of dried Coal F samples treated with 60% R.H. air.